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THE THERMAL NEUTRON ABSORPTION CROSS-SECTION OF ^{240}Pu*

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Oak Ridge, Tennessee, U.S.A.

(*Received* 24 *April* 1958)

Abstract—A measurement of the thermal neutron absorption cross-section of ^{240}Pu has been made using the Oak Ridge Pile Oscillator. Enriched ^{240}Pu samples and almost isotopically pure ^{239}Pu samples were compared with gold standards. All samples were sufficiently thin so as to offer negligible self protection. The ^{240}Pu was found to give a response per atom 2·94 times that of gold. Upon correcting for the non-$(1/v)$ character of ^{240}Pu absorption, a value of 285 ± 15 barns is computed for the 2200 m/sec absorption cross-section. The value of 314 ± 30 barns calculated from the resonance parameters of ^{240}Pu is in agreement with this measurement.

THE plutonium isotope of mass 240 will be produced in nuclear reactors containing ^{238}U (primarily via the path $^{239}Pu[n, \gamma]^{240}Pu$). The neutron cross-section of ^{240}Pu has therefore been of particular interest in predicting the formation of the higher isotopes, and in the estimation of the "burn-up" rate of the ^{240}Pu in the reactor. Accurate measurements of the absorption cross-section have been difficult to carry out prior to the availability of highly enriched ^{240}Pu samples, due to the large contribution to the absorption by ^{239}Pu. Furthermore, early activation measurements[1] of the thermal cross-section in reactors tended to be high compared to the thermal value because of the very large resonance (in excess of 10^5 barns) of ^{240}Pu at 1 eV. This latter resonance gives rise to a resonance integral for ^{240}Pu of about 9000 barns. Hence thin samples could exhibit effective reactor cross-sections based on the thermal flux several times their 2200 m/sec value, the exact value depending upon the ratio of resonance to thermal flux at the irradiation position. In this work the effective thermal absorption of highly enriched plutonium samples was measured with the Oak Ridge Pile Oscillator.[2,3] The measurement was carried out using a boron detector in a highly thermalized region (the reflector) of the Oak Ridge National Laboratory graphite reactor, where the ratio of resonance flux per ln (E) to thermal flux was about 0·001. All measurements were made relative to gold.

Two samples of PuO_2 (of isotopic composition 92·19% ^{240}Pu, 5·86% ^{239}Pu, 1·84% ^{241}Pu, and 0·11% ^{242}Pu) weighing 20·07 mg and 31·17 mg, respectively, were spread over about 10 cm² of aluminium foil so as to minimize self protection. The purified PuO_2 samples were spread as a slurry in D_2O to avoid protium contamination. Two additional samples of PuO_2 (of isotopic composition 99·78% ^{239}Pu, 0·19% ^{240}Pu and 0·03% ^{241}Pu) weighing 14·56 mg and 25·28 mg, respectively, were similarly

* This paper is based upon work performed for the United States Atomic Energy Commission at the Oak Ridge National Laboratory, operated by Union Carbide Corporation.

[1] P. R. FIELDS, G. L. PYLE, M. G. INGHRAM, H. DIAMOND, M. H. STUDIER and W. M. MANNING, *Nucl. Sci. Engng.* **1**, 62 (1956).
[2] J. I. HOOVER, W. H. JORDAN, C. D. MOAK, L. PARDUE, H. POMERANCE, J. D. STRONG and E. O. WOLLAN, *Phys. Rev.* **74**, 864 (1948).
[3] H. POMERANCE, *Phys. Rev.* **83**, 641 (1951).

spread on aluminium foils. Each of the plutonium samples and two blank aluminium foils (of weight equal to the aluminium in the plutonium samples) were sealed into matched magnesium containers in an identical manner, and oscillated in a beryllium boat. The response of each sample was compared with thin gold foils of almost equal response so that only minor interpolations were necessary. At least two separate measurements at different times were made on each of the Pu samples and the blanks. These data are summarized in Table 1.

TABLE 1.—PILE OSCILLATOR RESPONSE OF PLUTONIUM SAMPLES IN GOLD EQUIVALENCE

	Wt. of PuO_2 (mg)	Sample response equivalent to Au (mg)	$\frac{\text{Pu response}}{\text{Au response}}$ (corrected for isotopic composition)
^{240}Pu (1)	20·07	56·6, 57·1	2·99
^{240}Pu (2)	31·17	80·0, 83·5	2·88
^{239}Pu (1)	14·56	93·1, 92·3, 94·5	8·08
^{239}Pu (2)	25·29	155·9, 158·4	8·13
Blank (1)	—	7·4, 8·4	—
Blank (2)	—	8·6, 6·6	—

After subtracting the ^{239}Pu and ^{241}Pu contributions to the absorption in the ^{240}Pu sample (^{241}Pu was treated here as giving an equivalent response to ^{239}Pu), the ^{240}Pu was found to give a response per atom equivalent to 2·94 times that of Au. On the basis of $\sigma_{2200}(\text{Au}) = 99$ barns; a neutron width $\Gamma_n = 2{\cdot}24 \times 10^{-3}$ eV and a radiation width $\Gamma_\gamma = 37 \times 10^{-3}$ eV for the 1·055 eV resonance[4] in ^{240}Pu; and a thermal flux distribution characterized by a Maxwellian temperature of 450°K; it is computed that $\sigma_{2200}(^{240}\text{Pu}) = 285 \pm 25$ barns. The correction is primarily due to the deviation of ^{240}Pu absorption from $(1/v)$.

The above value may be compared to 460 ± 45 barns reported by KRUPCHITSKII,[5] 250 ± 35 barns reported by CORNISH and LOUNSBURY,[6] 340 ± 50 barns reported by STOUGHTON and HALPERIN[7] and a value of 314 ± 30 barns computed from resonance parameters.

Acknowledgements—The authors are indebted to J. MARTIN of the Electronuclear Division of Oak Ridge National Laboratory for making the enriched plutonium available, and particularly to R. W. STOUGHTON for many helpful discussions.

[4] D. J. HUGHES and R. B. SCHWARTZ, *Neutron Cross Sections*. Supplement 1, (BNL-325), (1957).
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[6] F. W. CORNISH and M. LOUNSBURY, Unpublished work (1956).
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THE RAMAN AND INFRA-RED SPECTRA AND STRUCTURE OF DI-(π*CYCLO*PENTADIENYLIRON) TETRACARBONYL

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(*Received* 12 *May* 1958)

THE infra-red spectrum of $[(C_5H_5)Fe]_2(CO)_4$ was first reported by PIPER *et al.*[1] several years ago. It was then possible to draw several conclusions quite directly from certain general features of the spectrum. Firstly, the general appearance of the spectrum between 6 and 15 μ suggested that the metal to ring bonding was of the sandwich type and, secondly, the appearance of a strong absorption band at $\sim$5·6 μ suggested that there was at least one bridging carbonyl group in addition to terminal CO groups, the latter giving rise to strong bands in the region 1950–2060 cm^{-1}. In a following paper,[2] a more detailed study of the CO stretching region, on both the dissolved and crystalline materials was reported. Concurrently with this second study of the infra-red, SHOEMAKER and WILSON[3] carried out a preliminary X-ray study which indicated very strongly that the molecules in the crystal are centrosymmetric. It was not entirely clear at that time that this was consistent with the infra-red spectrum of the crystalline material and it was pointed out[2] that it appeared impossible to reconcile the solution spectra, showing three strong CO stretching bands, with the persistence of a centrosymmetric structure in the dissolved molecules.

The molecular structure of $[(C_5H_5)Fe]_2(CO)_4$ in the crystalline state has now been determined in some detail by MILLS.[4] He finds that there are two ketonic bridging carbonyl groups, with these and the two iron atoms defining a plane. To each iron atom, above and below this plane, are attached a terminal CO group and a π-*cyclo*pentadienyl group, the entire molecule having a centre of symmetry.

We wish to suggest a reasonable though not absolutely certain interpretation of our previously reported[2] infra-red spectrum of the solid (see Table 1) on the basis of MILLS's results. In addition to the above details of molecular structure, he finds two non-equivalent molecular sites. A molecule with the centrosymmetric structure reported by MILLS would, on the basis of the usual selection rules, be expected to have one infra-red active absorption band due to the bridging carbonyl groups and one due to the terminal groups. There are in fact two pairs of strong bands, *viz.*, 1965–1950 and 1782–1770 cm^{-1}. It is reasonable to suppose that those at 1965 and 1950 are due to the infra-red active terminal modes in the two environmentally different molecules and those at 1782 and 1770 are due to the infra-red active bridging

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[1] T. S. PIPER, F. A. COTTON and G. WILKINSON, *J. Inorg. Nucl. Chem.* **1**, 165 (1955).
[2] F. A. COTTON, A. D. LIEHR and G. WILKINSON, *J. Inorg. Nucl. Chem.* **1**, 175 (1955).
[3] D. P. SHOEMAKER and F. C. WILSON, Private communication. Quoted in ref. 2.
[4] O. S. MILLS, Private communication.

modes in the two environmentally different molecules. The weak shoulder at ~2000 cm^{-1} may be due to a normally infra-red silent terminal mode in one of the two environmentally distinct molecules, which gains some intensity due to lattice effects.

In order to obtain further information about the symmetry and structure of the molecule in solution the infra-red spectrum in a number of solvents and the Raman

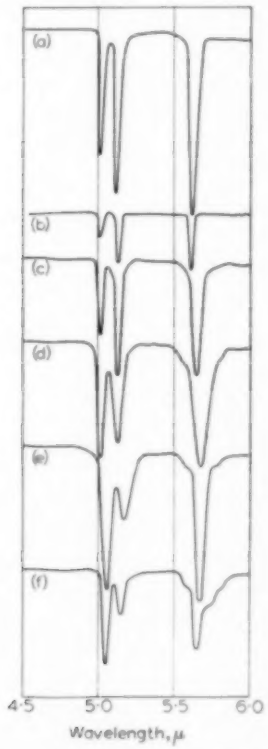

FIG. 1.—Infra-red spectrum of $(C_5H_5Fe)_2(CO)_4$ in various solvents:
(a) carbon disulphide
(b) hexane
(c) carbon tetrachloride
(d) chloroform
(e) pyridine
(f) ethyl alcohol

spectrum in several solvents have been studied. The infra-red spectra were taken in the range 4·5–6·0 μ using a calcium fluoride prism. The Raman spectrum was measured by techniques previously described by one of us[5] for compounds absorbing in the blue part of the visible region. All of these data are summarized in Table 1 and the infra-red spectra are illustrated in Fig. 1.

EXPERIMENTAL

Raman spectra. Samples consisted of 2 per cent solutions in chloroform and ethanol and 3 per cent in pyridine. The apparatus and general technique have been previously described by STAMMREICH.[5] The helium 6678·1 Å and 7065·2 Å lines were used for excitation and the spectra were recorded photographically. Even at these low concentrations, the samples showed appreciable absorption of the exciting lines (particularly 6678·1 Å); they were, however, fairly transparent for scattered radiation shifted to the CO stretching region. The helium line at 7281·3 Å, also present in the incident radiation, is of much lower intensity than He 6678·1 and

[5] H. STAMMREICH, *Spectrochim. Acta* **8**, 41 (1956).

TABLE 1.—INFRA-RED AND RAMAN SPECTRA OF $(C_5H_5Fe)_2(CO)_4$ IN THE CARBONYL STRETCHING REGION

Spectrum	Nature of sample	Absorption bands[b,c]				
		1900–2100 cm^{-1}			1700–1900 cm^{-1}	
Infra-red	Solid in KBr[a]	2000 (*sh*, *w*)		1965 (*vs*) 1950 (*vs*)	1782 (*vs*) 1770 (*vs*)	
	Soln in CS_2	2055 (*vw*)	2000 (*vs*)	1959 (*vs*)	1783 (*vs*)	
	Soln in *n*-hexane	—[d]	2001 (*vs*)	1958 (*vs*)	1786 (*vs*)	
	Soln in CCl_4	2056 (*vw*)	2002 (*vs*)	1958 (*vs*)	1774 (*vs*)	
	Soln in $CHCl_3$	2055 (*vs*)	2000 (*vs*)	1957 (*vs*)	1763 (*vs*)	
	Soln in pyridine	—[d]	1996 (*vs*)	1952 (*vs*)	1776 (*vs*)	
	Soln in C_2H_5OH	—[d]	1995 (*vs*)	1951 (*vs*)	1779 (*vs*)	1745 (*m*) 1724 (*vw*)
Raman	Solns in pyridine, $CHCl_3$ and EtOH	2064 (3,b)	2019 (2)	1958 (6)	1737 (3) 1721 (5)	

[a] As reported in reference 2.
[b] Band positions good to ± 5 cm in the infra-red and ± 4 cm^{-1} in the Raman.
[c] *vs*, very strong; *sh*, shoulder; *m*, medium; *vw*, very weak.
[d] See Experimental section under Infra-red Spectra.
Numbers in parentheses following Raman lines indicate relative intensities; b, broad.

7065·2 and, very probably, does not excite any observable Raman lines of the compound under the experimental conditions. We found, however, a number of Raman shifts of the solvents excited by He 7281·3 Å.

The most luminous possible optical arrangement was used, viz., a grating with 600 grooves/mm, blazed for first order wavelength of 7500 Å; camera 1: 2, $f=12$ cm; reciprocal dispersion 110 Å/mm; Kodak IN plates. All spectra were exposed 7 hr. Longer exposures were not feasible because of increasing turbidity of the samples (decomposition) and formation of small gas bubbles. The temperature of the samples during exposure was maintained between 8 and 12°. Polarization measurements were not possible.

Several factors induced us to limit ourselves to obtaining the Raman spectra only in the CO stretching region, but even in this region the quality of the recorded spectra is far below usual. The observed shifts are relatively weak compared with the background caused by stray light. We considered therefore only those Raman lines as probably genuine ones that were observed in the spectra of the compound in at least two different solvents. These very probably genuine shifts in cm^{-1} are the following: 1721 (5), 1737 (3), 1958 (6), 2019 (2), 2064 (3, broad).

Of these five shifts, the three strongest (1721, 1958, 2064 cm^{-1}) were observed as excited by both He 6678·1 Å and by He 7065·2 Å. They have to be considered therefore as the most certain ones. 2019 cm^{-1} was found to be excited by He 6678·1 Å in the spectra of all three solutions; this line is reasonably certain. 1737 cm^{-1} was observed only in the spectra of the chloroform and pyridine solutions and has to be

regarded as less certain than the other frequencies. However, the observed shift cannot be ascribed to a Raman frequency of the solvent and hardly to a Raman frequency of $(C_5H_5Fe)_2(CO)_4$ excited by any other He line. The latter possibility would presume one of the following fundamentals: 497 cm^{-1} (excited by He 7281 Å), 917 cm^{-1} (excited by He 7065 Å) or 3782 cm^{-1} (excited by He 5876 Å). The latter one can be excluded immediately and we found no evidence for one of the low frequency fundamentals.

Infra-red spectra. The spectra reported in this paper were obtained with a Baird double beam spectrometer using a calcium fluoride prism. Polystyrene film was used for calibration and the accuracy in the 4·5–6·0 μ range is $\pm$ 0·015 μ (~5 cm). The very weak infra-red band at 2050–2060 cm^{-1} was not observed in the present work, since the solutions used were too dilute to reveal it. However, it was previously observed[2] in CCl_4, $CHCl_3$ and CS_2. Saturated solutions in hexane are too dilute to permit its observation.

DISCUSSION

There appears now to be no doubt that in solid $(C_5H_5Fe)_2(CO)_4$ there exist discrete molecules which contain two bridging carbonyl groups and are centrosymmetric.[3,4] According to the interpretation which is given above, the infra-red spectrum of the solid is consistent with such a structure.

However, the infra-red data previously presented[1,2] and the more extensive data given here are clearly inconsistent with the existence of centrosymmetric molecules in the solutions studied as has been previously stated.[2] Further evidence for this conclusion is provided by a comparison of the infra-red and Raman spectra. It is a perfectly general theorem in the theory of molecular vibrations[6] that in a centrosymmetric molecule there can be no vibration which is both infra-red and Raman active. Inspection of Table 1 shows that in the 1900–2100 cm^{-1} range there are several infra-red–Raman coincidences. In particular the strong infra-red line at ~1958 cm^{-1} is coincident with the strongest Raman line at 1958 cm^{-1}. The Raman spectrum also has lines at 2019 and 2064 cm^{-1}; the former is quite close to the infra-red line at ~2000 cm^{-1} but need not necessarily be a coincidence. The 2064 cm^{-1} Raman line matches within experimental error the weak infra-red band at ~2055 cm^{-1}.

Comparison of the infra-red and Raman spectra in the 1700–1900 cm^{-1} range leads to a puzzling situation. It would seem that for any non-centrosymmetric structure a molecule of the stoicheiometry $(C_5H_5Fe)_2(CO)_4$ should also have coincident bridging carbonyl absorptions. As noted in the Experimental section the 1721 cm^{-1} Raman band is quite certain although the 1737 cm^{-1} could conceivably be spurious. Nevertheless the difference between the infra-red absorption (1775–1785 cm^{-1}) and the Raman shift (1721 cm^{-1}) is without any doubt too great to suggest other than that they are due to different vibrational modes.

The possibility of some relaxation of selection rules due to free rotation of the rings when the molecule is freed from the crystal lattice may be considered. Previous work[2] has indicated that this is not likely, nor does it appear possible to explain the present data in this way. Even if one were to assume that one of the two Raman lines, say the 1737 cm^{-1} line, is spurious and that the effect of rotation is such as to lift the selection rule for the terminal CO's but not for the bridging CO's, it would be

[6] See, for example, E. B. WILSON, JR., J. C. DECIUS and P. C. CROSS, *Molecular Vibrations*. McGraw-Hill New York (1955).

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impossible to account for the presence of three rather widely separated terminal CO stretching frequencies in a molecule containing only two terminal CO groups.

The possibility of there existing more than one molecular species in solution has been considered but it does not seem possible to suggest any definite hypotheses which would cleanly explain the data. For example, if one again presumed that 1737 cm^{-1} Raman line to be spurious, one might attribute the Raman lines at 1721 and 2091 cm^{-1} and the infra-red lines at $\sim$1780 and $\sim$2000 cm^{-1} to a centrosymmetric molecule of the type existing in the crystal and the Raman lines at 1958 and 2064 cm^{-1} and the infra-red lines at 1958 and $\sim$2055 cm^{-1} to some other species not containing bridging CO groups.

While still other hypotheses of varying degrees of plausibility might be suggested, we shall not attempt to account in detail for these spectral data. It is our purpose only to present the data and to point out that they seem to substantiate the idea that some change in molecular structure must occur when the molecule leaves the crystal lattice and goes into solution.

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THE STABILITIES AND ENTHALPIES OF DISSOCIATION OF SOME AMMINE COMPLEXES OF PLATINUM(II)

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Abstract—The dissociation pressures of a series of ammine complexes of platinum(II) were measured at various temperatures. These complexes, diammine (2:2′-bipyridine) platinum(II), 2:2′-bipyridinebis(methylamine)-platinum(II), 2:2′-bipyridine(ethylenediamine)platinum(II) and 2:2′-bipyridine-(1:3-diaminopropane)platinum(II) chlorides, dissociate, on heating, to give the gaseous ammine and dichloro(2:2′-bipyridine)platinum(II). Free energies, enthalpies and entropies of dissociation were calculated from the ammine dissociation pressures and the unexpected order of stability, $[Pt(bipy)tn]Cl_2 < [Pt(bipy)en]Cl_2 < [Pt(bipy)(NH_3)_2]Cl_2 < [Pt(bipy)(CH_3NH_2)_2]Cl_2$, was found. Possible causes of this anomalous order are discussed.

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IN the light of current interest in co-ordination chemistry and the need for quantitative data for further development in the field,[1] a programme was initiated for the investigation of the thermodynamic properties of the dissociation of a series of solid ammine platinum(II) complex compounds. It seemed desirable, in order to simplify the interpretation of the data, to study a system in which only two co-ordination sites were available and that these sites should be oriented to permit chelation.

Dichloro(2:2′-bipyridine)platinum(II), $[Pt(bipy)Cl_2]$, was selected for the investigation. This compound, which has been described by several authors[2,3] is very stable. The bipyridine base is tightly bound and is not readily displaced by other bases. The two chloro groups can easily be displaced by nitrogen bases, and since they occupy adjacent positions in the co-ordination sphere, both can be replaced by two monodentate ligands or a bidentate ligand. Preliminary investigations showed that bases which add to the compound, by replacing the chloro groups, may be rather easily removed on heating. The original $[Pt(bipy)Cl_1]$ is then recovered and has been found to be stable up to 200°C.

The following series of complexes were used in this study: diammine(2:2′-bipyridine)platinum(II)chloride, $[Pt(bipy)(NH_3)_2]Cl_2$; 2: 2′-bipyridine(dimethylamine) platinum(II)chloride, $[Pt(bipy)(CH_3NH_2)_2]Cl_2$; 2:2′-bipyridine (ethylenediamine) platinum(II)chloride, $[Pt(bipy)en]Cl_2$; and 2:2′-bipyridine (1:3-diaminopropane) platinum(II)chloride; $[Pt(bipy)tn]Cl_2$. The vapour-pressure of the ammine base over each of the solid complexes was measured as a function of temperature.

EXPERIMENTAL

Preparation of compounds. Dichloro(2:2′-bipyridine)platinum(II) was prepared by the method described by MORGAN and BURSTALL.[2] The ammine complexes of this compound were prepared by the addition of the anhydrous ammine to a chloroform suspension of $[Pt(bipy)Cl_2]$. The resulting mixture was stirred for 1–2 hr at

[1] R. S. NYHOLM, *Rev. Pure Appl. Chem.* **4**, 15 (1954).
[2] G. L. MORGAN and F. H. BURSTALL, *J. Chem. Soc.* 965 (1934).
[3] L. ROSENBLATT and A. SCHLEEDE, *Liebigs Ann.* **505**, 51 (1933).

room temperature until a distinct colour change occurred in the suspended solid (bright yellow to buff). The solid was collected on a fritted glass filter and was washed with acetone and then ether. The resulting solid contained up to two moles of ammine in excess of the necessary stoicheiometric amount. The excess ammine was removed by placing the complex over P_2O_5 in a vacuum. (Calc. for $[Pt(bipy)(NH_3)_2]Cl_2$; Pt, 42·78; C, 26·32; H, 3·09. Found: Pt, 42·92; C, 25·68; H, 3·08%. Calc. for $[Pt(bipy)(CH_3NH_2)_2]Cl_2$; Pt, 40·30; Cl, 14·64. Found: Pt, 40·28, Cl, 14·66%. Calc. for $[Pt(bipy)en]Cl_2$; Pt, 40·47; Cl, 14·70. Found: Pt, 40·37; Cl, 14·41%. Calc. for $[Pt(bipy)tn]Cl_2$; Pt, 39·32; Cl, 14·28. Found: Pt, 39·25; Cl, 14·30%.)

The gaseous ammine bases, ammonia and methylamine, used in the above preparations, were dried by condensing the anhydrous ammine on an excess of alkali metal (sodium and lithium respectively). The ammines were then recondensed on the chloroform suspensions and the resulting mixture was allowed to warm to room temperature. The diamine bases, ethylenediamine and 1:3-diaminopropane, were dehydrated and purified by the method described by ROLLINSON and BAILAR.[4]

X-ray powder patterns of the four ammine complexes and of the parent platinum compound were obtained. No simple correlation could be found between any of the patterns. The more intense lines of the five patterns were compared to the lines of a Hull–Davey chart for the tetragonal and hexagonal structures. The complex $[Ptbipy(NH_3)_2]Cl_2$ was so found to be tetragonal with $c/a = 0{\cdot}90$, $a = 21{\cdot}7$ Å and $c = 19{\cdot}5$ Å and the complex $[Pt(bipy)en]Cl_2$ was found to be tetragonal with $c/a = 1{\cdot}10$, $a = 24{\cdot}0$ Å and $c = 26{\cdot}4$ Å. Structures of the other compounds were not determined.

Apparatus and pressure measurements. The apparatus used for vapour-pressure measurements employed an isotenoscope of the "sickle gauge" type. The sickle gauge was constructed primarily according to the directions given by PHIPPS *et al.*[5] with the modification that two sickle bulbs were placed in series in the apparatus. Conventional high vacuum techniques were used, where possible, in the design, construction and operation of the apparatus. A constant temperature oil bath was used to control the temperature of the system.

Several independent pressure readings were obtained at each temperature for each complex studied. These readings consisted of balancing the pressure in a reference tube against that of the sample tube as indicated by the sickle gauge. The pressure in the reference tube was then obtained from an attached wide bore, closed end mercury manometer which was read with a high precision cathetometer. The pressure in the reference tube was then decreased slightly and then "rebalanced" to obtain an independent pressure reading.

The apparatus was calibrated at room temperature using various known pressures (in the same range as the experimental pressures). Several independent readings were obtained at each pressure. In all 30–50 measurements were obtained at 3–5 different pressures. The average error in the pressure readings obtained by this calibration was applied to the experimental vapour-pressure readings.

Differential thermal analyses of $[Pt(bipy)en]Cl_2$ and $[Pt(bipy)tn]Cl_2$ were run with Al_2O_3 and/or $[Pt(bipy)Cl_2]$ references by Mr. G. UEHARA of the Department of Soil Science at this University.

[4] C. L. ROLLINSON and J. C. BAILAR, *Inorganic Synthesis* Vol. 2, p. 197. Wiley, New York (1946).
[5] T. E. PHIPPS, M. L. SPEALMAN and T. G. COOK, *J. Chem. Educ.* **12**, 321 (1935).

RESULTS

The average values of the vapour-pressure measurements obtained at each temperature are listed in Table 1 with the statistically determined estimate of the standard

TABLE 1.—AVERAGE OBSERVED VAPOUR-PRESSURES

$[Pt(bipy)(NH_3)_2]Cl_2$		$[Pt(bipy)(CH_3NH_2)_2]Cl_2$		$[Pt(bipy)en]Cl_2$		$[Pt(bipy)tn]Cl_2$	
$t \pm 0.1$ (°C)	P (mm)	$t \pm 0.3$ (°C)	P (mm)	$t \pm 0.3$ (°C)	P (mm)	$t \pm 0.3$ (°C)	P (mm)
87·4	8·51 ± 0·17	78·3	10·12 ± 0·17	114·2	4·39 ± 0·27	89·1	9·25 ± 0·13
94·3	12·63 ± 0·19	82·2	16·27 ± 0·16	117·1	4·75 ± 0·13	97·0	11·22 ± 0·20
99·1	16·24 ± 0·17	85·6	23·16 ± 0·13	120·0	5·11 ± 0·10	102·3	12·14 ± 0·25
104·4	24·63 ± 0·19	89·0	29·71 ± 0·16	124·2	5·89 ± 0·17	107·9	12·95 ± 0·19
109·4	35·08 ± 0·11			129·0	6·44 ± 0·29	113·0	13·66 ± 0·25
				132·5	6·71 ± 0·14	122·2	14·04 ± 0·24

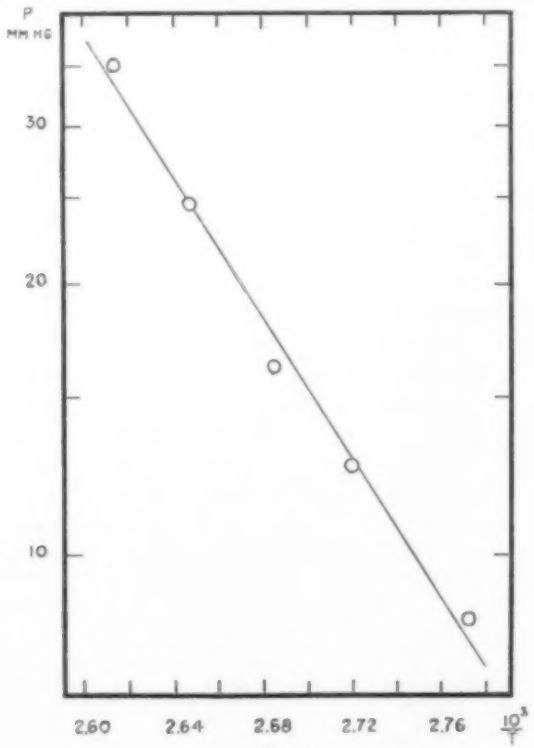

FIG. 1.

deviations. (Each value listed is the average of approximately 10 independent measurements.) The logarithms of average value for each complex at each temperature were plotted versus the inverse absolute temperature (e.g. Fig. 1). The data for that part of each curve which approached a straight line were treated according to standard

statistical methods to obtain the equation for the straight line. The resulting equations are of the form

$$\log P = A - B\left(\frac{10^3}{T}\right).$$

The pressures, in mm of Hg, the values of A and B and the estimates of the standard deviations are listed in Table 2 for each complex.

TABLE 2.—CONSTANTS FOR THE EQUATION LOG $P_{mm} = A - B(10^3/T)$

Compound	A	B	$\pm$	Valid temperature range
$[Pt(bipy)(NH_3)_2]Cl_2$	11·659	3·878 ± 0·059	0·022	87–110°C
$[Pt(bipy)(CH_3NH_2)_2]Cl_2$	17·486	5·791 ± 0·118	0·023	78–89°C
$[Pt(bipy)en]Cl_2$	5·675	1·951 ± 0·114	0·017	114–125°C
$[Pt(bipy)tn]Cl_2$	3·247	0·813 ± 0·051	0·009	97–108°C

It is assumed that the dissociation process is

$$[Pt(bipy)(Am)m]Cl_2(s) = [Pt(bipy)Cl_2](s) + n\text{Am}(g)$$

and the pressure which is measured over the solid complex is due to the liberated ammine (Am) vapour. The equilibrium constant for this process is defined

$$K = p^n$$

with p measured in atmospheres. From an extrapolation of the data to 25° and the thermodynamic relationships between equilibrium constant, free energy, enthalpy and entropy, the values of ΔF°, ΔH° and ΔS° for the dissociation processes were obtained. These data are listed in Table 3, with the estimates of the standard deviations.

TABLE 3.—THERMODYNAMIC DATA FOR THE DISSOCIATION PROCESS (AT 25°C)

Compound	ΔF° (kcal/mole)	ΔH° (kcal/mole)	ΔS° (cal/deg mole)
$[Pt(bipy)(NH_3)_2]Cl_2$	11·54 ± 0·12	35·49 ± 0·54	80·32 ± 1·85
$[Pt(bipy)(CH_3NH_2)_2]Cl_2$	13·16 ± 0·19	53·00 ± 1·10	133·6 ± 3·7
$[Pt(bipy)en]Cl_2$	5·12 ± 0·13	8·93 ± 0·52	12·8 ± 1·8
$[Pt(bipy)tn]Cl_2$	3·22 ± 0·05	3·72 ± 0·23	1·68 ± 0·81

These thermodynamic data are based upon the validity of the assumptions: (1) that the dissociation process is reversible, (2) that the expression for K is correct and (3) that ΔH° is constant over the temperature range of the extrapolation. While it was not positively demonstrated that the dissociation process is reversible, the evidence shows that the reverse process does occur but at a very slow rate. The equilibrium constant expression is based on accepted thermodynamic conventions concerning the activities of solid substances[6] and on the usual approximation that the fugacity of a gas is equal to its pressure at low pressures. The constancy of ΔH° will be considered later.

[6] S. GLASSTONE, *Thermodynamics for Chemists* pp. 291–2. Van Nostrand, New York (1947).

DISCUSSION

One should expect that the ΔH° for the dissociation of these complexes would be approximately equal, that ΔS° would be larger for the complexes containing the monodentate bases, and that the resulting increasing stability order would be $[Pt(bipy)(NH_3)_2]Cl_2$, $[Pt(bipy)(CH_3NH_2)_2]Cl_2$, $[Pt(bipy)tn]Cl_2$ and $[Pt(bipy)en]Cl_2$. The data in Table 3 show that the four complexes are in two distinct groups with $[Pt(bpy)(NH_3)_2]Cl_2$ and $[Pt(bipy)CH_3NH_2)_2]$ in one, characterized by high values of ΔH° and ΔS° and the remaining two complexes in the other group with unexpectedly low values of ΔH° and ΔS°. The apparent stability order is almost the reverse of the expected order. An explanation for the large differences in ΔH° and ΔS° between these two groups of complexes may help explain the anomalous stability order.

In comparing the thermodynamic constants for the dissociation of the complexes in this study, consideration of the following hypothetical exchange reaction will be helpful:

$$\underset{A}{[Pt(bipy)(Am)n]Cl_2(s)} + m\text{Bn(g)} = \underset{B}{[Pt(bipy)(Bn)m]Cl_2(s)} + n\text{Am(g)}$$

where Am and Bn are two different ammine bases and n or m is 1 or 2. Then, for the above type of reaction,

$$\Delta G^\circ_D = \Delta G^\circ_A - \Delta G^\circ_B$$

where ΔG° represents the thermodynamic quantities ΔF°, ΔH° or ΔS° and the subscripts refer to the dissociations of the corresponding complexes. From the following thermochemical cycle for the exchange reaction;

$$\begin{array}{lcl}
[Pt(bipy)(Am)n]Cl_2(s) + m\text{Bn(g)} & \xrightarrow{\Delta G_{\text{lattice}}} & [Pt(bipy)(Am)n]^{++}(g) + 2Cl^-(g) + m\text{Bn(g)} \\
\Big\downarrow {\scriptstyle \Delta G^\circ_D} & & \Big\downarrow {\scriptstyle \Delta G_{\text{bonding}}} \\
 & & [Pt(bipy)]^{++}(g) + n\text{Am(g)} + 2Cl^-(g) \\
 & & \Big\downarrow {\scriptstyle -\Delta G'_{\text{bonding}}} \qquad + m\text{Bn(g)} \\
[Pt(bipy)(Bn)m]Cl_2(s) + n\text{Am(g)} & \xleftarrow{-\Delta G'_{\text{lattice}}} & [Pt(bipy)(Bn)m]^{++}(g) + 2Cl^-(g) + n\text{Am(g)}
\end{array}$$

it follows that

$$\Delta G^\circ_D = \Delta G_{\text{lattice}} - \Delta G'_{\text{lattice}} + \Delta G_{\text{bonding}} - \Delta G'_{\text{bonding}}$$

The data for the exchange reactions are listed in Table 4.

The thermodynamic lattice constants for this series of complexes are not known. However, some semi-quantitative estimates can be made. KAPUSTINSKII[7] has given the following empirical equation for lattice energies, independent of crystal structure;

$$U = \frac{287{\cdot}2nZ_1Z_2}{r_1 + r_2}\left(1 - \frac{0{\cdot}34}{r_1 + r_2}\right)$$

where n is the number of ions, Z_1 and Z_2 are the ionic charges and r_1 and r_2 are the ionic radii. Using $n = 3$, $Z_1Z_2 = 2$, $r_2 = 1{\cdot}81$ Å (Cl^- radius) and a minimum value of 2·7 Å[8] for r_1 it can be shown that a difference in cationic radii of 0·7–0·8 Å is necessary to give a difference in lattice energies of 40–50 kcal, while 0·1–0·2 Å

[7] A. F. KAPUSTINSKII. *Acta Physicochem. U.R.S.S.* **18**, 370 (1943); *Chem. Abstr.* **38**, 5705 (1943).
[8] The cationic radius of 2·73Å for $[Pt(NH_3)_4]^{++}$ was calculated from the data of I. I. CHERNYAEV and V. A. POLKIN, *Zh. Neorg. Khim.*, **1**, 890 (1956); *Chem. Abstr.* **51**, 3266 (1956).

difference results in a 5–10 kcal lattice energy difference. Lattice entropies have been shown by ALTSHULLER[9] to agree within 5 cal/deg per mole for various series of simple salts. In this consideration, for a series of similar compounds, a large difference in lattice energies between the compounds should be accompanied by a

TABLE 4.—THERMODYNAMIC CONSTANTS FOR THE EXCHANGE REACTION
$[Pt(bipy)(Am)n]Cl_2(s) + mBn(g) = [Pt(bipy)(Bn)m]Cl_2(s) + nAm(g)$

nAm − mBn	ΔF°_D	ΔH°_D	ΔS°_D
$2NH_3$–$2CH_3NH_2$	−1·62	−17·51	−53·3
$2NH_3$–en	6·42	26·56	67·5
$2NH_3$–tn	8·32	31·77	78·6
$2CH_3NH_2$–en	8·04	44·07	120·8
$2CH_3NH_2$–tn	9·94	49·28	131·9
en–tn	1·90	5·21	11·1

correspondingly large difference in lattice free energies and not in the lattice entropies. Some other explanation must be sought for the anomalies in the experimental data.

To explain these data it is necessary to propose that the complexes in the two groups differ in some marked way. One possible difference could occur in the manner in which the ligand molecules are bound within the complex; e.g. they might be co-ordinated directly to the platinum in one case forming a normal complex and be bound loosely in the other case (solvate formation). However, in this model, the vapour-pressures of the solvate compounds would be expected to be higher, at a given temperature, than those of the normal complexes. An alternate possibility is that the four complexes in this series are normal complexes, as previously assumed, except that the difunctional ligands are bonded to the platinum through only one amine group. In this model the diamine would function only as a monodentate ligand and, as such, the complexes containing these diamine ligands should have vapour-pressures comparable to those monoammine complexes in the same temperature range. This model may be modified slightly by assuming that the diamine ligands function as bidentate ligands at lower temperatures, but at higher temperatures one of the Pt–N bonds is broken. Then the diamine acts as a monodentate ligand. When the amine bond is broken, the enthalpy and entropy of the solid increase, which would account for the much lower values of ΔH° and ΔS° of dissociation of these complexes. The breaking of the first Pt–N bond would not be detected by the experimental method used. This latter model is proposed as being most satisfactory to explain the data for the chelate complexes. Differential thermal analysis of the ethylenediamine and diaminopropane complexes, with Al_2O_3 or $[Pt(bipy)Cl_2]$ as the reference standards were made. The resulting curves show that two transitions occur below 200°C, the first of which begins between 80° and 100°C and probably corresponds to the breaking of the first Pt–N bond. The second transition begins between 130° and 150°C and corresponds to the dissociation of the amine from the complex.

A comparison of the enthalpies of bonding ($\Delta H_{\text{bonding}}$) for the complexes in this series can be obtained from ΔH°_D values if the lattice energy terms are known or can

[9] A. P. ALTSHULLER, *J. Chem. Phys.* **26**, 404 (1957)

otherwise be treated in a quantitative or semi-quantitative way. For the complexes containing the ammonia and methylamine bases, assuming equal lattice energies for these complexes, the enthalpy of bonding per ligand is 8·75 kcal ($\frac{1}{2}\Delta H_D^\circ$) greater for the latter complex. This is predicted qualitatively by the relative basicities of the two ligands, since methylamine is more basic than is ammonia. The 8·75 kcal difference is only a lower limit, because the lattice energy of the methylamine complex may be less than that of the ammonia complex (assuming a slighter largly cationic radius for the methylamine complex).

For the complexes containing the ethylenediamine and diaminopropane bases, again assuming equal lattice energies for these complexes, the enthalpy of bonding per ligand molecule is 5·21 kcal (ΔH_D°) greater for the ethylenediamine complex. This is in qualitative disagreement with the enthalpies of bonding predicted by the relative basicities of the two bases, since the diaminopropane is more basic than the ethylenediamine. However, the lattice energy of the diaminopropane complex should be less than that of the ethylenediamine complex and the 5·21 kcal difference in the enthalpies of bonding is an upper limit and may be due to a large difference in the lattice energies.

In the proposed model for the chelate complexes, it can be further assumed that when the first Pt–N bond is broken a chloride ion present in the solid complex becomes co-ordinated to the platinum. The conditions for the use of the Kapustinskii equation are altered since the number of ions and the ionic charges are altered. No simple relation can be offered concerning lattice energies of the complexes in the two groups. However, assuming equal cationic radii for the complexes in both groups, the lattice energies of these complexes, with $Z_1 = Z_2 = 1$, are one-third those of the monoammine complexes. This shows that lattice energy differences are a major contribution to ΔH_D° when comparing the two groups of complexes.

A major contribution to ΔS° for the dissociation of each of the four complexes should come from the entropy of the liberated ammine base. The standard entropies of two moles of methylamine and ammonia are 115·5 and 92·0 e.u. respectively.[10] The standard entropies of ethylenediamine and 1:3-diaminopropane are estimated to be 64·3 and 74·5 e.u. respectively.[11] Comparison of these values with ΔS° for the dissociation process for the corresponding complexes shows that for the methylamine and ammonia complexes, the major contribution to ΔS° is, indeed, the entropy of the liberated ammonia or amine. With the other two complexes, the increase in entropy due to the liberated amine bases seems to be offset by a large increase in the entropies of the solid substances involved in the process.

For the calculation of the thermodynamic constants from the vapour-pressure data it was assumed that ΔH° is constant over the extrapolated temperature range. The ethylenediamine and diaminopropane complexes under the proposed model, are the hypothetical complexes at 25°, with one Pt–N bond broken, and hence the ΔH° values are for the hypothetical complexes and not chelate complexes.

Acknowledgement—The authors wish to thank the U.S. Atomic Energy Commission, which supported this research at Michigan State University.

[10] F. D. ROSSINI, D. D. WAGNER, W. H. EVANS, S. LEVINE and I. JAFFE, *Selected Values of Chemical Thermodynamic Properties* N.B.S. Circular 500 (1952).
[11] Estimated by the method of ANDERSON, BEYER and WATSON as described by I. M. KLOTZ, *Chemical Thermodynamics* pp. 172–8. Prentice Hall, New York (1950).

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SPECTROPHOTOMETRIC STUDIES ON THIOCYANATOCUPRATE(II) COMPLEXES IN AQUEOUS SOLUTION

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Abstract—The formation constants of thiocyanatocuprate(II) complexes have been determined spectrophotometrically in aqueous solution. The overall formation constants K_n^c for $Cu(SCN)_n^{2-n}$ at an ionic strength of 0·5 at 25°C were found to be 55·1, 347, 490 and 970 for $n = 1$, 2, 3 and 4, respectively. The thermodynamic constants at 25° for $Cu(SCN)^+$ and $Cu(SCN)_2$ were calculated to be 200 and 4480, respectively, from the concentration constants obtained at ionic strengths of 0·05 and 0·1 at 25°C. These values are compared with the formation constants of other thiocyanato complexes.

IRVING and WILLIAMS,[1] in their excellent review, state that comparisons of the stabilities of complexes of different ligands are most effective when metals of the same type are used. They compared the stability data of bivalent metals of the first transition series and found that the order $Mn < Fe < Co < Ni < Cu > Zn$ is valid irrespective of the nature of the co-ordinated ligands or the number of ligands involved. The series was correlated with the ionic radii and the sum of the first and the second ionization potentials of these metals.

As for the complexes with inorganic ligands co-ordinated, IRVING and WILLIAMS took into consideration the complexes which contain cyanide, hydroxide, sulphate and thiosulphate ions as co-ordinating groups. Among them, the complexes with cyanide and sulphate ions do not satisfy the above order. Such an irregularity may be explained in view of the acidity of the co-ordinating groups, because the acidity affects the stability of the complex.[2] Since the thiocyanate ions have comparably strong acidity,[3] it might be interesting to compare with the stabilities of thiocyanato complexes of bivalent metal ions from the view-point of the rule proposed by IRVING and WILLIAMS.

So far, the thiocyanato complexes with cobalt(II),[4] nickel(II),[5] zinc(II)[6] and copper(II)[7] have been studied quantitatively. The formation constants given to those complexes with the first three metal ions are sound, while those given to the complexes with copper(II) seem to be too high, which were determined by OUDINET and GALLAIS[7] in water–acetone media.

The reinvestigation of the thiocyanatocuprate(II) complexes, therefore, seemed to be worth while in order to confirm the validity of the viewpoint of IRVING and WILLIAMS. In the present paper are given the formation constants of thiocyanatocuprate(II)

[1] H. IRVING and R. J. P. WILLIAMS, *J. Chem. Soc.* 3192 (1953).
[2] A. E. MARTELL, *J. Phys. Chem.* **59**, 308 (1955).
[3] G. S. LAURENCE, *Trans. Faraday Soc.* **52**, 236 (1956).
[4] M. LEHNÉ, *Bull. Soc. Chim. Fr.* 76 (1951).
[5] S. FRONAEUS, *Acta Chem. Scand.* **7**, 21 (1953).
[6] R. E. FRANK and D. N. HUME, *J. Amer. Chem. Soc.* **75**, 1736 (1953).
[7] M. OUDINET and F. GALLAIS, *Compt. Rend. 78e Congr. Socs. savantes Paris et depts., Sect. sci.* 373 (1953).

complexes which were determined spectrophotometrically in aqueous solution of various ionic strengths.

EXPERIMENTAL

Apparatus. Hitachi Spectrophotometer Model EPU-2 with quartz absorption cells of 10 mm and 100 mm in length of light path was used for the absorption measurement. The pH of the solution was measured with Hitachi pH-meter Model EHP-1 with a glass electrode.

The temperature of the cell compartment was regulated within two degrees by circulating the water of appropriate temperature and by means of an electric heater attached on the bottom of the cell compartment.

Standard solutions. The cupric nitrate solution was prepared by dissolving a known amount of electrolytic copper metal (99·99 per cent pure) into redistilled nitric acid, removing the excess of nitric acid by gentle heating and diluting with distilled water to 1 M in concentration. The potassium thiocyanate solution was prepared from a guaranteed reagent after recrystallization from distilled water,[8] the concentration of which was determined by argentimetry. The potassium nitrate solution was also prepared from a guaranteed reagent, but without further purification.

Procedures. Sample solutions were prepared by mixing distilled water and known quantities of the standard solutions of cupric nitrate and potassium thiocyanate in a volumetric flask. The ionic strength of the solutions was adjusted with potassium nitrate. The sample solution which was preliminarily kept in a thermostat to equilibrate its temperature was filled into a quartz absorption cell. The absorption was measured in the range of wave numbers of 10,000 to 40,000 cm^{-1} at ionic strengths of 0·05, 0·1 and 0·5 at 20° and 25°C. A reference cell for the absorption measurement was filled with a solution of the same composition except one of cupric and thiocyanate ions which was lower in concentration than the other in the sample solution, so that the absorption of the complexes present in the sample solution was directly measured with this procedure.

The absorption maximum of the complexes was found to shift to some extent with change in pH of the solution. The location of the maximum and the absorbancy at the maximum, however, remained constant irrespective of pH unless the pH of the solution was greater than 3·5. In this study, therefore, the pH of the solution was adjusted to be between 2·8 and 3·5.

At concentration of thiocyanate in higher than 0·1 M a white-yellow precipitate was observed appearing in the solution, when the absorbancy decreased gradually with lapse of time. On the other hand, no change was observed in absorbancy at lower concentrations of thiocyanate ion. In the former case, the true value of absorbancy was obtained by plotting the absorbancy observed against time and by extrapolating the plot to a zero time.

RESULTS

Absorption curves of copper(II) solution which were obtained in the absence and the presence of thiocyanate ions are reproduced in Fig. 1.* Free cupric ions give absorption maxima of low intensity at wave numbers of 33,000 cm^{-1} and 13,200 cm^{-1}.

* In the present paper absorbancy is expressed as the values per 1 cm light path.

[8] I. M. KOLTHOFF and J. J. LINGANE, *J. Amer. Chem. Soc.* **57**, 2126 (1935).

Upon addition of thiocyanate the absorption at greater wave number increased to a great extent and its maxima shifted to wave numbers of 27,800 cm^{-1} to 29,200 cm^{-1} depending on the concentration of thiocyanate added, while the absorption at smaller wave number gave no remarkable change.

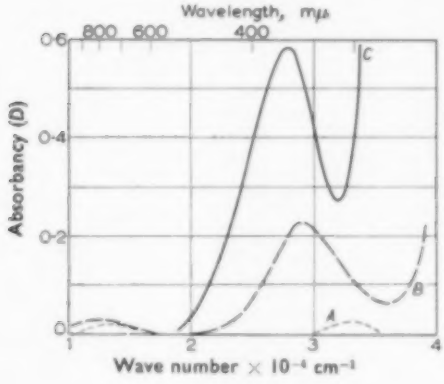

FIG. 1.—Absorption curves of free cupric ion and mixtures of cupric and thiocyanate ions at 25° and at ionic strengths of 0·1 for *A* and *B*, and 1·0 for *C*.
A, 2×10^{-3} M $Cu(NO_3)_2$;
B, 2×10^{-3} M $Cu(NO_3)_2 + 5 \times 10^{-3}$ M KSCN;
C, 2×10^{-3} M $Cu(NO_3)_2 + 0{\cdot}91$ M KSCN.

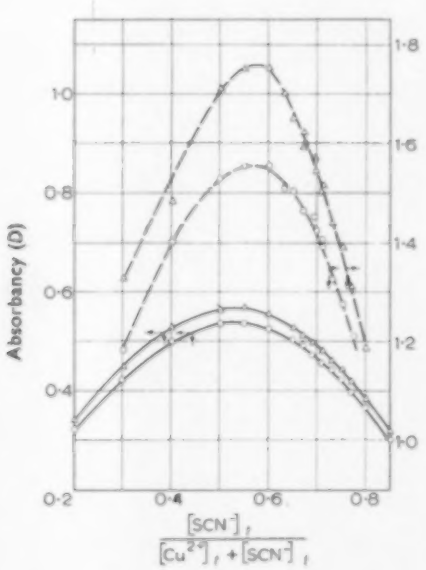

FIG. 2.—Relation between *D* and $[SCN^-]_t/([Cu^{2+}]_t + [SCN^-]_t)$ obtained for thiocyanatocuprate(II) complexes by the method of continuous variation at wave numbers of 27,800 cm^{-1} (○) and 29,200 cm^{-1} (△), at 25° and at an ionic strength of 0·1: full line, $[Cu^{2+}]_t + [SCN^-]_t = 0{\cdot}01$ M; broken line, $[Cu^{2+}]_t + [SCN^-]_t = 0{\cdot}02$ M.

Thiocyanatocuprate(II) complexes may be written as $Cu(SCN)_n^{2-n}$ ($n = 1, 2, 3$ and 4), because the co-ordination number of copper(II) complexes is generally considered to be four.[9] Applying the method of continuous variation[10] to three different systems in which the sums of total copper and total thiocyanate concentrations were 0·005 M, 0·01 M and 0·02 M, it was found that the species of $Cu(SCN)^+$ predominates. However, the presence of $Cu(SCN)_2$ may not be neglected especially in the solution of 0·02 M. In Fig. 2 are shown some typical examples.

[9] A. E. MARTELL and M. CALVIN, *Chemistry of Metal Chelate Compounds* p. 243. Prentice-Hall, New York (1952).
[10] P. JOB, *Ann. Chim.* (II) **6**, 97 (1936).

Besides $Cu(SCN)^+$ which forms through the reaction,

$$Cu^{2+} + SCN^- \rightleftharpoons Cu(SCN)^+, \tag{1}$$

higher species, $Cu(SCN)_2$, $Cu(SCN)_3^-$ and $Cu(SCN)_4^{2-}$, may be produced with the increase of the concentration of thiocyanate according to the following reactions.

$$Cu(SCN)^+ + SCN^- \rightleftharpoons Cu(SCN)_2 \tag{2}$$

$$Cu(SCN)_2 + SCN^- \rightleftharpoons Cu(SCN)_3^- \tag{3}$$

$$Cu(SCN)_3^- + SCN^- \rightleftharpoons Cu(SCN)_4^{2-} \tag{4}$$

The successive formation constant k_n ($n = 1, 2, 3$ and 4), expressed in terms of molar concentration, is defined for each species by the equation,

$$k_n = \frac{[Cu(SCN)_n^{2-n}]}{[Cu(SCN)_{n-1}^{3-n}]\,[SCN^-]}, \qquad (n = 1, 2, 3 \text{ and } 4). \tag{5}$$

When the total concentration of copper(II) in the solution, a, is in a large excess over the total concentration of thiocyanate, b, $Cu(SCN)^+$ is the only species present in the solution, of which the concentration c_1 is expressed by the equation,

$$c_1 = k_1 (a - c_1)(b - c_1) = k_1 ab/(1 + ak_1), \tag{6}$$

If the Beer's law holds, the absorbancy D is given by,

$$D = \epsilon_1 c_1 = \epsilon_1 k_1 ab/(1 + ak_1), \tag{7}$$

where ϵ_1 means the molar extinction coefficient of $Cu(SCN)^+$. Rearranging equation (7),

$$\frac{ab}{D} = \frac{a}{\epsilon_1} + \frac{1}{\epsilon_1 k_1} \tag{8}$$

is obtained.

From a series of experiments which were carried out at varied concentrations of thiocyanate up to $2{\cdot}5 \times 10^{-4}$ M but at the concentrations of copper(II) fixed to $0{\cdot}7 \times 10^{-2}$ and $2{\cdot}0 \times 10^{-2}$ M, it was found that the Beer's law holds under the experimental conditions, the plot of absorbancy D against the concentration of total thiocyanate being linear as shown in Fig. 3.

Another series of experiments were made at varied concentrations of copper(II) but at the concentration of thiocyanate fixed to 1×10^{-4} M, with the results given in Table 1. From those results the values of ab/D were plotted against the concentration of copper(II) as shown in Fig. 4, from which k_1 and ϵ_1 were determined.

In the medium of the appropriate concentration of thiocyanate, two species, $Cu(SCN)^+$ and $Cu(SCN)_2$, are significant, when k_1 and k_2 are expressed by the equations,

$$k_1 = \frac{c_1}{(a - c_1 - c_2)(b - c_1 - 2c_2)} \quad \text{and} \quad k_2 = \frac{c_2}{c_1(b - c_1 - 2c_2)}, \tag{9}$$

where c_2 represents the concentrations of $Cu(SCN)_2$. When $b \gg a$, the above equations can be simplified, so that the absorbancy D is given by equation (10).

$$D = \epsilon_1 c_1 + \epsilon_2 c_2 = \frac{a(\epsilon_1 k_1 b + \epsilon_2 k_1 k_2 b^2)}{1 + k_1 b + k_1 k_2 b^2}, \tag{10}$$

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TABLE 1.—ABSORPTION MEASUREMENT FOR THE DETERMINATION OF k_1 AND ϵ_1

$a \times 10^3$ (M)	$D_{obs.}$*	$ab/D_{obs.} \times 10^5$†
$\mu = 0.05$		
0.800	0.0207	3.86
1.000	0.0236	4.24
1.200	0.0255	4.71
1.400	0.0273	5.13
1.600	0.0292	5.48
$\mu = 0.10$		
0.800	0.0184	4.35
1.000	0.0214	4.67
1.400	0.0245	5.71
1.800	0.0282	6.38
2.000	0.0292	6.85

* Measured at 29200 cm^{-1}.
† b was fixed to 1.000×10^{-4} M.

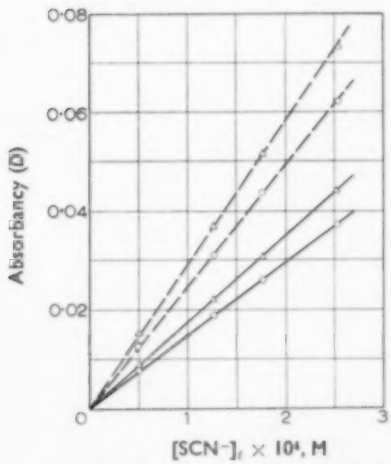

FIG. 3.—Relation between D and $[SCN^-]_t$ obtained for thiocyanatocuprate(II) complexes at the constant concentration of total copper(II), being measured at wave numbers of 27,800 cm^{-1} (○) and 29,200 cm^{-1} (△), at 20° and at an ionic strength of 0·1: full line, 0.7×10^{-2}M $[Cu^{2+}]_t$; broken line, 2.0×10^{-2} M $[Cu^{2+}]_t$.

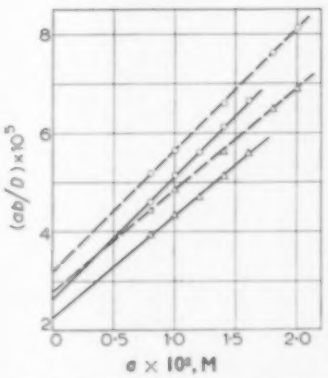

FIG. 4.—Plots of ab/D vs. a obtained at wave numbers of 27,800 cm^{-1} (○) and 29,200 cm^{-1} (△), at ionic strengths of 0·05 (full line) and 0·1 (broken line) and at 25°. The concentration of total thiocyanate is 1×10^{-4} M.

where ϵ_2 represents the molar extinction coefficient of $Cu(SCN)_2$. From equation (10) is obtained

$$\frac{1}{b^2k_1} + \frac{1}{b} - \frac{a\epsilon_1}{Db} = \frac{a}{D}\epsilon_2 k_2 - k_2. \tag{11}$$

Using equation (10), Beer's law was examined, with the result that a linear relation was obtained between D and a when b was kept constant. The value of the left-hand

side of equation (11) was plotted against a/D as shown in Fig. 5, from which ϵ_2 and k_2 were calculated.

Taking the third species $Cu(SCN)_3^-$ into consideration, equations (12) and (13) are derived.

$$D = \frac{a(\epsilon_1 k_1 b + \epsilon_2 k_1 k_2 b^2 + \epsilon_3 k_1 k_2 k_3 b^3)}{1 + k_1 b + k_1 k_2 b^2 + k_1 k_2 k_3 b^3}. \tag{12}$$

$$\frac{1}{b^3 k_1 k_2} + \frac{1}{b^2 k_2} - \frac{1}{b} - \frac{a\epsilon_1}{Db^2 k_2} - \frac{a\epsilon_2}{Db} = \frac{a}{D}\epsilon_3 k_3 - k_3. \tag{13}$$

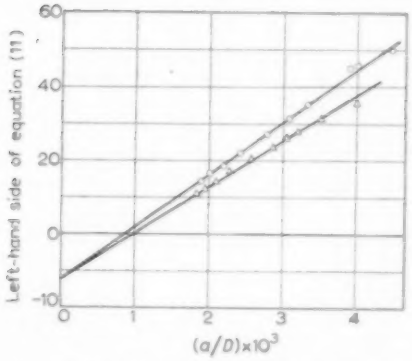

FIG. 5.—Plots of the left-hand side of equation (11) vs. a/D obtained at wave numbers of 27,800 cm^{-1} (○) and 29,200 cm^{-1} (△), at an ionic strength of 0·1 and at 25°. a was fixed to 1×10^{-4} M and b was varied in the concentration range of $0{\cdot}8 \times 10^{-3}$ M to $4{\cdot}0 \times 10^{-2}$ M.

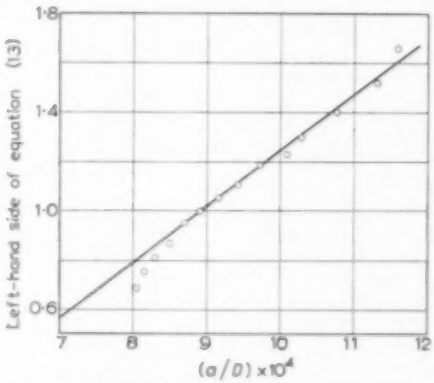

FIG. 6.—Plots of the left-hand side of equation (13) vs. a/D obtained at a wave number of 27,800 cm^{-1}, at an ionic strength of 0·5 and at 25°. a was fixed to 4×10^{-4} M and b was varied in the concentration range of 0·14 M to 0·36 M.

The left-hand side of equation (13) was plotted against a/D with the values obtained at higher concentrations of thiocyanate, which is shown in Fig. 6 and from which ϵ_3 and k_3 were calculated.

At higher concentrations of thiocyanate the plot given in Fig. 6 tends to deviate from the straight line predicted from equation (13), which occurs when b exceeds 0·32 M. This discrepancy was considered to arise from the fact that the fourth species of thiocyanatocuprate(II) complex, $Cu(SCN)_4^{2-}$, actually existed in the solution.

Taking into consideration the existence of all four species of thiocyanatocuprate(II) complex, the equation,

$$D = \frac{a(\epsilon_1 k_1 b + \epsilon_2 k_1 k_2 b^2 + \epsilon_3 k_1 k_2 k_3 b^3 + \epsilon_4 k_1 k_2 k_3 k_4 b^4)}{1 + k_1 b + k_1 k_2 b^2 + k_1 k_2 k_3 b^3 + k_1 k_2 k_3 k_4 b^4} \tag{14}$$

was derived. From the values of absorbancy observed under two different conditions, ϵ_4 and k_4 were calculated by means of equation (14).

The results obtained for thiocyanatocuprate(II) complexes in aqueous solution are summarized in Table 2, where overall formation constants K_n^c are written instead of successive ones. The calculation by the method of least squares indicated that the probable errors for K_1^c are 1·8 per cent at $\mu = 0{\cdot}05$ and 1·3 per cent at $\mu = 0{\cdot}1$. Although it seems difficult to calculate accurately the probable errors for K_2^c, K_3^c and K_4^c, those are presumed as approximately 5 per cent for K_2^c and more than 10 per cent for K_3^c and K_4^c.

TABLE 2.—OVERALL FORMATION CONSTANTS AND MOLAR EXTINCTION COEFFICIENTS OF THIOCYANATOCUPRATE(II) COMPLEXES IN AQUEOUS SOLUTIONS

Formation constant K_n^c					Molar extinction coefficient ϵ_n		
	Temp. (°C)	Ionic strength				Values at wave number of 29,200 cm^{-1}	Values at wave number of 27,800 cm^{-1}
		0·05	0·1	0·5			
K_1^c	20	102	84·9	—	ϵ_1	477	389
	25	96·9	79·6	55·1			
K_2^c	20	1980	1390	—	ϵ_2	967	1210
	25	1490	995	347			
K_3^c	25	—	—	490	ϵ_3	—	2000
K_4^c	25	—	—	970	ϵ_4	—	1000

Using the concentration constants obtained at ionic strengths of 0·05 and 0·1, the thermodynamic formation constants K_1 and K_2 for $Cu(SCN)^+$ and $Cu(SCN)_2$ were calculated with the relations,

$$K_1 = K_1^c \frac{f_{Cu(SCN)^+}}{f_{Cu^{2+}} . f_{SCN^-}} \quad \text{and} \quad K_2 = K_2^c \frac{f_{Cu(SCN)_2}}{f_{Cu^{2+}} . f_{SCN^-}^2},$$

where K_1^c and K_2^c mean the concentration constants for $Cu(SCN)^+$ and $Cu(SCN)_2$, respectively, and f's, the activity coefficients of corresponding species. In the calculation the activity coefficients of cupric and thiocyanate ions were taken from the KIELLAND's table[11] and that of $Cu(SCN)_2$ was assumed to be unity. The activity coefficient of $Cu(SCN)^+$ was evaluated by comparing two values of concentration constant K_1^c obtained at 0·05 and 0·1, from which the ion size parameter of $Cu(SCN)^+$ in the Debye–Hückel equation was calculated with the result of a reasonable value of 4 Å.

The values calculated for K_1 and K_2 were 200 and 4480, respectively. The free energy changes for the reactions,

$$Cu^{2+}\,(aq.) + SCN^-\,(aq.) = Cu(SCN)^+\,(aq.)$$

and

$$Cu^{2+}\,(aq.) + 2SCN^-\,(aq.) = Cu(SCN)_2\,(aq.)$$

were calculated to be −3·14 kcal/mole and −4·98 kcal/mole, respectively.

DISCUSSION

The solutions which were subjected to the absorption measurement contained a large quantity of potassium nitrate, being added to adjust the ionic strength thereof. However, the nitrate ion has only such a small tendency to form a complex with copper(II) ion[12] that it seems unnecessary to consider the effect of nitrate on our procedure of calculation.

The round maxima on the curve obtained by the method of continuous variation (Fig. 2) was in accordance with the fact that the formation constant of $Cu(SCN)^+$ is considerably small.

[11] J. KIELLAND, *J. Amer. Chem. Soc.* **59**, 1675 (1937).
[12] J. BJERRUM, *Chem. Rev.* **46**, 381 (1950).

In Table 3, the formation constants which have been reported for the thiocyanato complexes of silver(I),[13] mercury(II),[14] cadmium(II),[15] zinc(II),[6] cobalt(II),[4] nickel(II),[5] copper(II),[7] iron(III),[3] chromium(III)[16] and uranium(IV)[17] are summarized together with our values for thiocyanatocuprate(II) complexes. All of

TABLE 3.—OVERALL FORMATION CONSTANTS OF VARIOUS THIOCYANATO COMPLEXES

Metal ion	K_1^c	K_2^c	K_3^c	K_4^c	Experimental conditions		Ref.
					Temp. (°C)	Ionic strength	
Ag(I)	—	$2{\cdot}45 \times 10^3$	$4{\cdot}14 \times 10^3$	$7{\cdot}86 \times 10^3$	25	0	13a
	—	—	—	$6{\cdot}42 \times 10^3$	25	0	13b
Hg(II)	—	—	—	2×10^{19}	18	—	14
Cd(II)	11	56	6	60	30	2·0	15
Zn(II)	3	7	1	20	30	2·0	6
Co(II)	0·92	0·2	1	1000	—	—	4
Ni(II)	15	44	65	—	20	1·5	5
Cu(II)	—	—	$1{\cdot}5 \times 10^5$	3×10^6	18	$Mg(NO_3)_2$ 0·7 M	7
	55·1*	347*	490*	970*	25*	0·5*	
Fe(III)	139	2780	—	—	25	0·5	3
Cr(III)	74	960	—	—	25	>1	16
U(IV)	31	130	—	—	25	2	17

* Values obtained in the present investigation.

those constants given in Table 3 exist between 0·2 and 3000, except extremely high values for Ag(I), Hg(II) and the values for Cu(II) obtained by OUDINET and GALLAIS.[7] The formation constants of thiocyanatocuprate(II) complexes obtained in this study are much smaller than those by OUDINET and GALLAIS. This disagreement may be explained from the following facts: One is that OUDINET and GALLAIS determined the formation constants in acetone–water mixtures and the other is that they did not consider the existence of $Cu(SCN)_2$ species in the solution.

The thiocyanic acid is a strong acid,[3] and therefore it is not necessary to take into consideration a reaction such as depending on the pH of the solution,

$$HSCN + Cu^{2+} \rightleftharpoons CuSCN^{+} + H^{+}.$$

The value of 4 Å, calculated for the ion-size parameter of $Cu(SCN)^+$, seems reasonable, compared with 5·4 Å for that of $Fe(SCN)^{2+}$ obtained by LAURENCE.[3] This fact supports the validity of the formation constants of thiocyanatocuprate(II) complexes presented in this paper.

The magnitude of the first formation constants for thiocyanate complexes of cobalt(II),[4] nickel(II),[5] copper(II) and zinc(II)[6] in Table 2 are in accordance with the IRVING's order: $Co < Ni < Cu > Zn$. Although those values were obtained

[13] (a) G. C. B. CAVE and D. N. HUME, *J. Amer. Chem. Soc.* **75**, 2893 (1953);
(b) H. TAKAHASHI, Presented at the General Meeting of the Chem. Soc. Japan in Sendai, May, 1956.
[14] I. A. KORSHNOV and M. K. SHCHENNIKOVA, *Zh. Obshchel Khim.* **19**, 1820 (1949).
[15] D. D. DEFORD and D. N. HUME, *J. Amer. Chem. Soc.* **73**, 5321 (1951).
[16] K. G. POULSEN, J. BJERRUM and I. POULSEN, *Acta Chem. Scand.* **8**, 921 (1954).
[17] R. A. DAY, R. N. WILHITE and F. D. HAMILTON, *J. Amer. Chem. Soc.* **77**, 3180 (1955).

under different experimental conditions, the comparison mentioned above is still considered valid, because the ionic radii of those metal ions are almost identical[11] and the temperature coefficients of the formation constant and the change in the activity coefficients of the ion species[18] are not sufficiently great to reach an alternative conclusion.

It might be interesting to note the fact that the molar extinction coefficients of thiocyanato complexes of copper(II), nickel(II)[19] and cobalt(II)[19] decrease in the order of $Co > Ni > Cu$, which is directly opposite to the order of IRVING's rule.

[18] B. E. CONWAY, *Electrochemical Data* pp. 77–78. Elsevier, Amsterdam (1952).
[19] L. I. KATZIN, *J. Chem. Phys.* **20**, 1165 (1952).

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J. Inorg. Nucl. Chem., 1959, Vol. 9 pp. 24 to 31. Pergamon Press Ltd. Printed in Northern Ireland

ACETAMID ALS NICHTWÄSSRIGES IONISIERENDES LÖSUNGSMITTEL—I

KONDUKTOMETRISCHE TITRATIONEN IN GESCHMOLZENEM ACETAMID

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Abstract—Molten acetamide as a non-aqueous ionizing solvent acts in a pronounced way as a water-analogue. It shows a good or even very good ability to dissolve inorganic and organic compounds and it forms numerous stable solvates. According to the supposed mechanism of self-dissociation (autoprotolytic reaction) there can be defined acid- and base-analogues reacting in a way analogous to neutralizations. These neutralizations were followed conductometrically and by acid-base-indicators. In the case of Ag- and Cu-acetamide amphoteric phenomena could be shown by conductometric titrations.

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DAS geschmolzene Acetamid sollte sich aus zwei Gründen in besonderem Masse als wasserähnliches Lösungsmittel verhalten: Einmal bewirkt die Einführung der Acetylgruppe in das NH_3-Molekül eine Abschwächung des basischen Charakters und eine Verschiebung der Eingenschaften in Richtung auf das im Vergleich zu Ammoniak stärker saure Wasser (Tabelle 1) und andererseits lässt die hohe Dielektrizitätskonstante ein dem Wasser entsprechendes gutes Löse- und Ionisierungs vermögen erwarten.

TABELLE 1

NH_3 (sehr gross) → H_2O (15,7) → HF (3,2)
↘ ↘
CH_3CONH_2 (15,1) CH_3COOH (4,7)

(Die Werte in Klammern sind die negativen Logarithmen der Säuredissoziationskonstanten der betr. Verbindungen in Wasser)

Über die Dielektrizitätskonstante des geschmolzenen Acetamid liegen bisher nur zwei ältere Angaben vor, die beträchtlich voneinander abweichen (WALDEN,[1] ε^{83} 59,1; SCHAUM und HOLLA,[2] ε^{80} 65,3). Aus diesem Grunde wurde von uns die DK mit einem Dipolmeter (Wissenschaftl.-Techn. Werkstätten, Wessobrunn/Obb.; Messfrequenz: 1,8 MHz, Messprinzip: Schwebungsmethode) neu bestimmt zu ε 60,6 bei 94,0°, 62,4 bei 86,8° und 63,3$_5$ bei 83,2°. Eine Extrapolation liefert für 83° ε 63,4, für 80° ε 64,2. Die gefundene Temperaturabhängigkeit der DK $\frac{100}{\varepsilon}\left(\frac{\partial\varepsilon}{\partial t}\right) = 0{,}40$ stimmt gut überein mit der von Formamid $\left[\frac{100}{\varepsilon}\left(\frac{\partial\varepsilon}{\partial t}\right) = 0{,}35\right]$.[3]

[1] P. WALDEN, *Z. Physik. Chem.* **46**, 103 (1903).
[2] K. SCHAUM und HOLLA, *Liebigs Ann.* **542**, 77 (1939).
[3] G. R. LEADER, *J. Amer. Chem. Soc.* **73**, 856 (1951).

Als Ursache für die im Vergleich zu seinem Dipolmoment von 3,7 D [4] abnorm hohe DK muss eine Assoziation des geschmolzenen Acetamid über intermolekulare Wasserstoffbrücken angenommen werden. Aus verschiedenen Untersuchungen über die Struktur des flüssigen Acetamid[5–8] kann zusammenfassend gefolgert werden, dass sich die Assoziation des Acetamid erstreckt von der Bildung kettenförmiger Polymerer unter Bindung des trans-H-Atoms über die evtl. Verschmelzung von Dimeren unter Beteiligung des zweiten Elektronenpaares am O-Atom und über andere willkürliche Zwischentypen, bei denen sich zu einem beträchtlichen Grade die Beiträge jedes einzelnen Moleküls zum Gesamtdipolmoment der polymeren Gruppe wechselseitig aufheben, bis zu einem Dimeren von kleinem Moment bzw. dem Moment Null. Die beobachtete DK ist das Resultat der sich überlagernden Effekte all dieser verschiedenen Assoziationskomplexe.

Eine Bestätigung dafür liefert der Vergleich der Dielektrizitätskonstanten von Acetamid [ε^{94} 60,6; hypothetische DK im flüssigen Zustand bei 25° aus den DK-Werten von Acetamidlösungen wachsender Konzentration in Formamid zu ε^{25} 74 extrapoliert[5]], N-Methylacetamid (hypothetische DK im flüssigen Zustand bei 25° zu ε^{25} 183,3 extrapoliert) und N·N-Dimethylacetamid (ε^{25} 37,8). Die DK-Werte der N-Monoalkylamide sind beträchtlich grösser als die DK-Werte der unsubstituierten Amide, weil bei den Monoalkylderivaten wegen des Vorhandenseins von nur zwei Zentren, die sich an einer Wasserstoffbrückenbindung beteiligen können, und wegen der trans-Anordnung dieser Zentren die Bildung linearer Kettenassoziate begünstigt ist.[7]

Bei den N·N-Dialkylderivaten dagegen ist eine Assoziation über Wasserstoffbrücken überhaupt nicht mehr möglich und deshalb erfolgt ein starker Abfall der DK-Werte.

Die im Vergleich zu Acetamid wesentlich grössere DK von Formamid (ε^{25} 110) deutet darauf hin, dass der Gehalt an Dimeren bzw. an den vorstehend beschriebenen Zwischentypen in Acetamid grösser ist als in Formamid, analog dem Unterschied der Dielektrizitäts konstanten von Ameisensäure (ε^{25} 57) und Essigsäure (ε^{25} 6), der mit einem grösseren Dimerisationsgrad der Essigsäure erklärt wird.

Es soll noch darauf hingewiesen werden, dass sich für Acetamid beim Übergang vom flüssigen zum kristallinen Zustand, ähnlich wie bei Wasser, infolge der Änderung des Assoziationszustandes Veränderungen im Infrarotspektrum ergeben, wie sich auch das Spektrum des Kristallacetamid in den Solvaten von dem des reinen flüssigen bzw. festen Acetamid unterscheidet.[5]

Aus Untersuchungen von STAFFORD[9] und GRÜTTNER[10] geht hervor, dass die Löslichkeit anorganischer Verbindungen in geschmolzenem Acetamid etwa der in Wasser parallel geht, dass jedoch das Lösevermögen für organische Verbindungen im Vergleich zu Wasser wesentlich grösser ist.

Die Existenz zahlreicher Solvate der Alkali- und Erdalkalihalogenide,[8] der Mineralsäuren (vgl. experimenteller Teil), sowie von $HgCl_2$,[10] $AgNO_3$ und $Pb(NO_3)_2$[11] deutet bereits darauf hin, dass Acetamid ausser dem grossen Lösevermögen auch ein beträchtliches Ionisierungsvermögen besitzen wird.[12]

1. EIGENDISSOZIATION DES LÖSUNGSMITTELS, EXISTENZ VON SÄUREN- UND BASENANALOGEN UND KONDUKTOMETRISCHE VERFOLGUNG VON NEUTRALISATIONSREAKTIONEN

Nach Reinigung wird das Acetamid als völlig geruchloses, nicht mehr hygroskopisches Produkt mit einer spezifischen Leitfähigkeit $\varkappa_0^{94} = 2{,}6\text{–}4{,}0 \cdot 10^{-6}$ Ohm^{-1} cm^{-1} erhalten [zum Vergleich die niedrigsten $\varkappa_0$-Werte anderer Autoren: WALDEN[1]

[4] W. D. KUMLER und C. W. PORTER, *J. Amer. Chem. Soc.* **56**, 2549 (1934).
[5] W. D. KUMLER, *J. Amer. Chem. Soc.* **57**, 600 (1935).
[6] M. J. COPLEY, C. F. ZELLHOEFER und C. S. MARVEL, *J. Amer. Chem. Soc.* **60**, 2666 (1938).
[7] G. R. LEADER und J. F. GORMLEY, *J. Amer. Chem. Soc.* **73**, 5731 (1951).
[8] L. KAHOVEC und K. KNOLLMÜLLER, *Z. Physik. Chem.* **51B**, 49 (1941).
[9] O. F. STAFFORD, *J. Amer. Chem. Soc.* **55**, 3987 (1933).
[10] B. GRÜTTNER, *Z. Anorg. Chem.* **270**, 223 (1952).
[11] P. T. DANILTSCHENKO und W. G. EDIGER, *Ann. Inst. Anal. Phys. Chim.* **7**, 225 (1935); *C.* **I**, 4551 (1936).
[12] G. KORTÜM, *Lehrb. der Elektrochemie* pp. 121 ff., 223. Verlag Chemie (1957).

bei 81° $2{,}9 \cdot 10^{-4}$; WALKER und JOHNSON[13] bei 100° $4{,}3 \cdot 10^{-5}$; BELLADEN[14] bei 90° $1{,}5 \cdot 10^{-5}$; GRÜTTNER[10] bei 94° $8{,}6 \cdot 10^{-6}$].

Für den von GRÜTTNER[10] bereits diskutierten Mechanismus der Eigendissoziation des Lösungsmittels gemäss Gleichung (1)

$$2\,CH_3CONH_2 \rightleftharpoons CH_3CONH_3^+ + CH_3CONH^- \qquad (1)$$

(= Autoprotolysereaktion) spricht die Tatsache, dass Acetamid sowohl in stark sauren Medien (Essigsäure, Schwefelsäure) ein Proton aufnehmen kann,[15–18] andererseits in stark basischem Medium (flüssiges Ammoniak) ein Proton abgeben kann.[19–21]

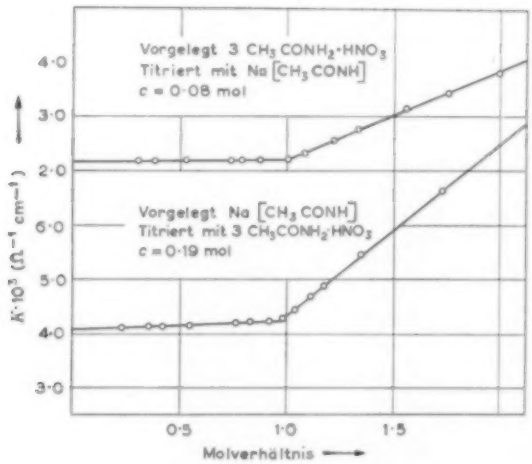

ABB 1.—Konduktometrische Titration von Acetamid-Nitrat mit Na-Acetamid und umgekehrt.

Die gemäss Gleichung (1) zu definierenden[22] Säurenanalogen (Mineralsäuren, Carbonsäuren) und Basenanalogen (Metallverbindungen des Acetamid, sowie N-Basen als potentielle Basen) setzen sich in Neutralisationsreaktionen unter Bildung des Lösungsmittels Acetamid und des betr. Salzes um. Derartige Reaktionen wurden von GRÜTTNER[10] konduktometrisch verfolgt und die entstandenen Salze isoliert.

Es sind dazu noch folgende Ergänzungen zu machen:

(a) Neutralisations-Titrationen können in Acetamid auch mit Hilfe von Säure-Basen-Indikatoren verfolgt werden. So reagiert Phenolphthalein wie in wässriger Lösung mit einer scharfen Farbänderung farblos → rotviolett bei Erreichen des

[13] J. W. WALKER und F. M. G. JOHNSON, *J. Chem. Soc.* **87**, 1597 (1905).
[14] L. BELLADEN, *Gazz. Chim. Ital.* **57**, 407 (1927).
[15] N. F. HALL, *J. Amer. Chem. Soc.* **52**, 5115 (1930).
[16] A. HANTSCH, *Chem. Ber.* **64**, 667 (1931).
[17] H. H. SISLER, A. W. DAVIDSON, R. STOENNER und L. L. LYON, *J. Amer. Chem. Soc.* **66**, 1888 (1944).
[18] A. R. GOLDFARB, A. MELE und N. GUTSTEIN, *J. Amer. Chem. Soc.* **77**, 6194 (1955).
[19] E. C. FRANKLIN und C. A. KRAUS, *Amer. Chem. J.* **23**, 277 (1900).
[20] E. C. FRANKLIN und O. F. STAFFORD, *Amer. Chem. J.* **28**, 83 (1902).
[21] E. C. FRANKLIN, *J. Amer. Chem. Soc.* **37**, 2279 (1915).
[22] G. JANDER, *Die Chemie in wasserähnlichen Lösungsmitteln* (1949).

alkalischen Gebietes (im Rahmen der Messgenauigkeit liegt der Umschlagspunkt genau am Äquivalenzpunkt); die Indikatoren Methylorange, Methylrot und Kongorot zeigen dagegen eine kontinuierliche Farbänderung, die keine genaue Endpunktsbestimmung gestattet.

(b) Salpetersäure bildet mit Acetamid zwei Solvate, $3CH_3CONH_2 \cdot HNO_3$ und $CH_3CONH_2 \cdot HNO_3$ (vgl. experimenteller Teil). Die von GRÜTTNER[10] gefundene Unstimmigkeit bei der Titration von Na-Acetamid mit Acetamid-Nitrat (und

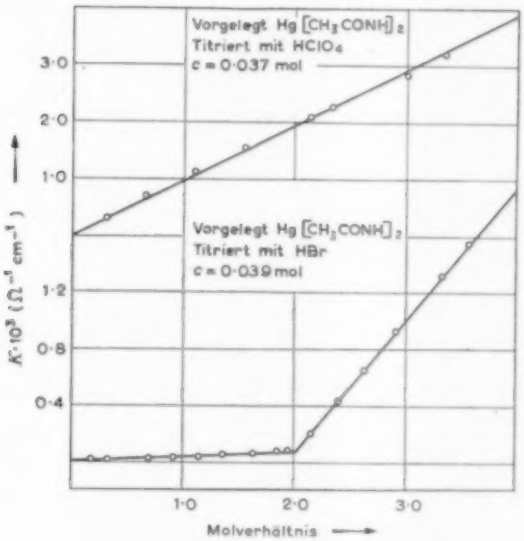

ABB. 2.—Konduktometrische Titration von Hg-Acetamid mit $HClO_4$ bzw. HBr.

umgekehrt) konnte von uns nicht beobachtet werden. Bei beiden Titrationen lag der Knickpunkt in der konduktometrischen Titrationskurve genau am Äquivalenzpunkt (Abb. 1). Es muss angenommen werden, dass das von Grüttner verwendete Acetamid-Nitrat $3CH_3CONH_2 \cdot HNO_3$ mit der 1:1-Verbindung verunreinigt war.

(c) Die extrem schwache Base $Hg[CH_3CONH]_2$ lässt sich mit $HClO_4$ oder HNO_3 überhaupt nicht titrieren. Mit HCl oder HBr dagegen wird eine normale Titrationskurve erhalten, da bis zum Äquivalenzpunkt die Bildung der nur wenig dissoziierten Hg^{II}-Halogenide $HgCl_2$ bzw. $HgBr_2$ erfolgt und erst nach dem Äquivalenzpunkt die Leitfähigkeit infolge des Überschusses an Halogenwasserstoff stark ansteigt (Abb. 2).

Die geringe Dissoziation des HgJ_2 und seine Neigung zur Komplexbildung gestattet die Darstellung von starken Basenanalogen gemäss Gleichung (2).

$$Hg[CH_3CONH]_2 + 4J^- \rightleftharpoons [HgJ_4]^{2-} + 2[CH_3CONH]^- \qquad (2)$$

In Abb. 3 ist die konduktometrische Titration des durch doppelte Umsetzung aus $Hg[CH_3CONH]_2$ und überschüssigem $[N(C_2H_5)_4]J$ in Lösung dargestellten Basenanalogen Tetraäthylammoniumacetamid mit $HClO_4$ wiedergegeben.

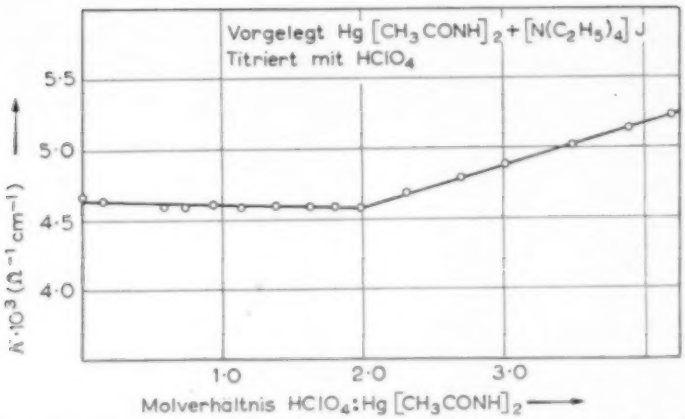

ABB. 3.—Konduktometrische Titration des durch doppelte Umsetzung aus $Hg[CH_3CONH]_2$ und $[N(C_2H_5)_4]J$ in Lösung erhaltenen Tetraäthylammoniumacetamid mit $HClO_4$.
Lösungsmittel: 15,00 g
Vorgelegt: 78,8 mg Hg-Acetamid + 788,6 mg $[N(C_2H_5)_4]J$
äquiv. Menge: 108,8 mg $2CH_3CONH_2.HClO_4$

2. KONDUKTOMETRISCHE UNTERSUCHUNG DES AMPHOTEREN VERHALTENS VON Ag- UND Cu-ACETAMID

GRÜTTNER und JANDER[23] stellten in einer Diskussion über die Amphoterie in Wasser und verschiedenen nichtwässrigen Lösungsmitteln fest, dass sowohl die

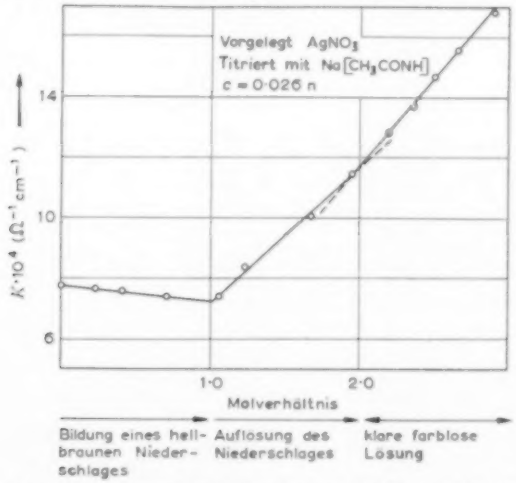

ABB. 4.—Konduktometrische Titration von $AgNO_3$ mit Na-Acetamid.

Auflösung von Hydroxyden in starker Lauge wie auch die Amphoterieerscheinungen in nichtwässrigen Lösungsmitteln von einem übergeordneten Gesichtspunkt aus als komplexchemische Vorgänge betrachtet werden müssen.

Aus qualitativen Untersuchungen ergibt sich für die schwerlöslichen Metallacetamidverbindungen des Ag, Cu^{II}, Pb^{II}, Pb^{IV} und Sn^{II}, die aus dem jeweiligen löslichen Metallsalz durch Umsetzung mit $Na[CH_3CONH]$ erhalten werden, eine Reihe

[23] B. GRÜTTNER und G. JANDER, *Z. Anorg. Chem.* **268**, 229 (1952).

zunehmender Neigung zur Komplexbildung mit überschüssigem $Na[CH_3CONH]$: $Sn^{II} < Pb^{IV} < Pb^{II} < Cu, Ag$.

Die Komplexbildung gibt sich durch die Auflösung der schwerlöslichen Niederschläge und/oder durch charakteristische Farbänderungen zu erkennen.

Für $Ag[CH_3CONH]$ und $Cu[CH_3CONH]_2$ kann man auf Grund des Verbrauches von 1 bzw. 2 Mol Alkaliacetamid pro Mol Metallacetamid bis zur Auflösung des Niederschlages auf die stöchiometrische Zusammensetzung der entstehenden Komplexverbindungen schliessen (Gleichungen 3 und 4).

$$Ag[CH_3CONH] + Na[CH_3CONH] \rightleftharpoons Na[Ag(CH_3CONH)_2] \quad (3)$$

$$Cu[CH_3CONH]_2 + 2Na[CH_3CONH] \rightleftharpoons Na_2[Cu(CH_3CONH)_4] \quad (4)$$

Eine Bestätigung der beiden Reaktionsgleichungen liefert die konduktometrische

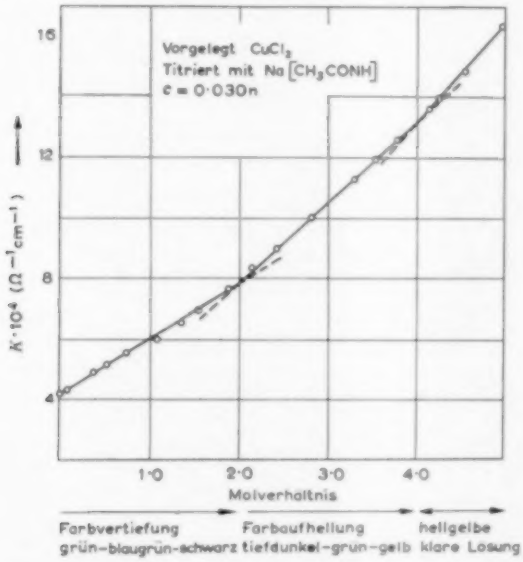

Abb. 5.—Konduktometrische Titration von $CuCl_2$ mit Na-Acetamid.

Verfolgung der Umsetzung von $AgNO_3$ und $CuCl_2$ mit $Na[CH_3CONH]$ (Abb. 4 und 5).

Die aus $PbCl_2$ und $(NH_4)_2[PbCl_6]$ mit $Na[CH_3CONH]$ erhaltenen Niederschläge gehen erst bei starkem Überschuss von $Na[CH_3CONH]$ (4–7 Mol pro Mol Metallacetamid) wieder in Lösung, während Sn-Acetamid auch mit einem grossen Überschuss von Alkaliacetamid nur teilweise gelöst wird.

Lösungen von Mg-, Al-, Sn^{IV}-, Fe-, Co- und Ni-Salzen geben mit Na-Acetamid keine Niederschläge.

3. EXPERIMENTELLER TEIL

Die Reinigung des verwendeten Acetamid erfolgte durch einmalige Vakuumdestillation des in den meisten Fällen stark nach Essigsäure riechenden Handelsproduktes (Merck) und anschliessende Umkristallisation der Hauptfraktion aus absolutem

Dioxan. Die erhaltenen groben Kristalle wurden zwei Tage bei 75° und 15 mm über Silicagel (Blaugel) getrocknet [F. 80,5–82,0° (unkorr.); $\varkappa_0^{94}$ 2,6–4,0 · 10^{-6} Ohm^{-1} cm^{-1}].

Eine wiederholte Vakuumdestillation dieses Produktes mit anschliessender doppelter Umkristallisations ua Dioxan verändert den $\varkappa_0$-Wert nicht. Jedoch tritt eine Erhöhung von $\varkappa_0$ auf 1,0–1,5 · 10^{-5} ein, wenn die Trocknung unter den beschriebenen Bedingungen nicht mit Silicagel sondern mit P_2O_5 vorgenommen wird.

Die Darstellung der für die Titrationen und Umsetzungen verwendeten basenanalogen Alkaliverbindungen des Acetamid erfolgte nach einer abgeänderten Vorschrift von GRÜTTNER.[10] Wegen der langen Zeit, die zur Herstellung relativ geringer Mengen nach Grüttner erforderlich ist, empfiehlt es sich, auf die vollständige Umsetzung des Alkalimetalls zu verzichten und die Reaktionstemperatur gerade so weit zu erhöhen, dass es nicht zu einer NH_3-Entwicklung und damit zur Bildung von Alkalidiacetamid kommt.

Zur Darstellung von Na-*Acetamid*, $Na[CH_3CONH]$, wurden 15 g reines und trocknes Acetamid in 300 ml absolutem Dioxan (über metall. Na getrocknet, unter N_2 abdestilliert, mit reinem Na-Acetamid nachbehandelt und unter Luftausschluss filtriert) gelöst, fünf Na-Kugeln von ca. 1,5–2,0 cm Durchmesser, die unter absolutem Dioxan blankgeschmolzen wurden, zugegeben und anschliessend 16 Stunden bei maximal 65° in einer N_2-Atmosphäre heftig gerührt. Danach wurde unter N_2-Spülung das nicht umgesetzte Na herausgenommen und weitere 8 Stunden bei 65° gerührt, um evtl. mechanisch abgeriebene Na-Flitter restlos umzusetzen. Das Reaktionsprodukt wurde unter Luftabschluss filtriert, zweimal mit heissem absoluten Dioxan gewaschen und auf der Fritte des Filtrationsapparates im Vakuum anfangs über Silicagel, dann über P_2O_5 getrocknet.

Rein weisses, hygroskopisches Pulver, Ausbeute 75%. Analyse: $N_{ber.}$ 17,28%, $N_{gef.}$ 17,2% (die N-Bestimmungen wurden nach Kjeldahl durchgeführt).

Entsprechend wurde K-*Acetamid*, $K[CH_3CONH]$, durch Umsetzung von 16,4 g Acetamid in 300 ml absolutem Dioxan mit zwei blanken K-Kugeln erhalten. Es wurde 6 Stunden bei maximal 40–50° unter N_2 gerührt, das nicht umgesetzte Kalium nach dieser Zeit herausgenommen und weitere 12 Stunden bei 40° gerührt. Das Produkt wurde wie vorstehend isoliert und getrocknet. Rein weisses, stark hygroskopisches Pulver, Ausbeute 59%. Analyse: $N_{ber.}$ 14,42%, $N_{gef.}$ 14,4%.

Die Darstellung von Hg-*Acetamid*, $Hg[CH_3CONH]_2$, erfolgte nach einer abgeänderten Methode von SCHOELLER und SCHRAUTH.[24] 25 g reines Acetamid wurden mit 60 g gelbem HgO in 350 ml Wasser 1 Stunde gekocht und das nicht umgesetzte HgO wurde durch dreimaliges Filtrieren entfernt (zurück: 35 g HgO). Das gelbgrün gefärbte klare Filtrat wurde im Vakuum auf dem Wasserbad zur Trockne eingedampft und der schwach gelb gefärbte Rückstand ¼ Stunde mit 25 ml Äthanol gekocht, der Alkohol abdekantiert und der Rückstand 6 Stunden im Extraktionsapparat mit Benzol extrahiert (die klare gelbgrün gefärbte Lösung darf zur Entfärbung nicht über Al_2O_3 oder Aktivkohle filtriert werden, da unter diesen Bedingungen eine Umwandlung in das wasserunlösliche CH_3CONH–HgOH eintreten kann; vgl. PREISS[25]). Rein weisses Produkt, Ausbeute 60% (bezogen auf eingesetztes Acetamid). Analyse: $Hg_{ber.}$ 63,34%, $Hg_{gef.}$ 63,0% (nach Biltz als HgS gefällt und bei 110° getrocknet).

[24] W. SCHOELLER und W. SCHRAUTH, *Ber. Dtsch. Chem. Ges.* **42**, 784 (1909).
[25] J. M. PREISS, *Colloid. J.* **3**, 795 (1937); *C.* **I**, 4891 (1939).

Die als säurenanaloge Verbindungen fungierenden Acetamidsolvate der Mineralsäuren wurden wie folgt erhalten:

Acetamid-Hydrochlorid, $2CH_3CONH_2 \cdot HCl$, Darstellung nach STRECKER,[26] Ausbeute an reinem Produkt 35%, F. 130,3–131,7° (aus Aceton/Äthanol) [in der Literatur angegebener F. 131°],[8] Analyse $N_{ber.}$ 18,12%, $Cl_{ber.}$ 22,93%, $N_{gef.}$ 18,1%, $Cl_{gef.}$ 23,3% (Chlorid nach Volhard);

Acetamid-Hydrobromid, $2CH_3CONH_2 \cdot HBr$, Darstellung erfolgte nach einer abgeänderten Vorschrift von WERNER,[27] 35 g reines Acetamid wurden in 180 ml Äthanol gelöst und mit 150 ml Äther verdünnt, zu der auf −50° abgekühlten Lösung wurden 25 ml konz. Bromwasserstoffsäure (66% ig, D 1,74) hinzugegeben, nach einigem Stehenlassen wurde der gebildete weisse kristalline Niederschlag abfiltriert und aus Aceton/Äthanol umkristallisiert, Ausbeute an reinem Produkt 30%, F. 140,0–142,0° [in der Literatur angegebener F. 138°],[28] Analyse $N_{ber.}$ 14,05%, $Br_{ber.}$ 40,15%, $N_{gef.}$ 14,0%, $Br_{gef.}$ 40,0% (Bromid nach Volhard);

Acetamid-Nitrat, 3 : 1-Verbindung, $3CH_3CONH_2 \cdot HNO_3$, Darstellung nach SRETCKER[26] aus 45 g reinem Acetamid und 19 ml konz. HNO_3, Ausbeute an reinem Produkt 25%, F. 69,5–71,0° (Aceton), Analyse $N_{ber.}$ 17,49%, $NO_{3\,ber.}$ 25,81%, $N_{gef.}$ 17,5%, $NO_{3\,gef.}$ 25,7% (NO_3 mit Nitron nach Busch);

Acetamid-Nitrat, 1 : 1-Verbindung, $CH_3CONH_2 \cdot HNO_3$, diese bisher nicht beschriebene Verbindung wurde durch Umsetzung von 20 g Acetamid mit 60 ml konz. HNO_3 dargestellt, das Reaktionsprodukt wurde zweimal aus je 20 ml Aceton umkristallisiert (bei Verwendung von weniger Aceton zersetzte sich ein Präparat ohne erkennbare äussere Ursache spontan beim Umkristallisieren), grobe Kristalle, Ausbeute an reinem Produkt 31%, F. 98,8–99,3°, Analyse $N_{ber.}$ 11,47%, $NO_{3\,ber.}$ 50,79%, $N_{gef.}$ 11,4%, $NO_{3\,gef.}$ 50,3%;

Acetamid-Perchlorat, $2CH_3CONH_2 \cdot HClO_4$, Darstellung nach GRÜTTNER[10] aus 100 g rohem Acetamid und 80 ml 70% ig. $HClO_4$, Ausbeute an reinem Produkt 22%, F. 89,7–90,7° (aus wenig Aceton), Analyse $N_{ber.}$ 12,82%, $ClO_{4\,ber.}$ 45,50%, $N_{gef.}$ 12,8%, $ClO_{4\,gef.}$ 45,4% (ClO_4 mit Nitron nach Busch).

Eine ausführliche Beschreibung der für die Leitfähigkeitsmessungen benutzten Messanordnung wird in der 3. Mitt. über die Leitfähigkeit und Stärke von Elektrolyten in Acetamid gegeben.[29]

Die Durchführung der vorliegenden Arbeit wurde durch Gewährung von ERP-Mitteln in grosszügiger Weise gefördert, wofür wir an dieser Stelle danken.

[26] A. STRECKER, *Liebigs Ann.* **103**, 321 (1857).
[27] A. WERNER, *Ber. Dtsch. Chem. Ges.* **36**, 154 (1903).
[28] A. HANTSCH und F. E. DOLLFUSS, *Ber. Dtsch. Chem. Ges.* **35**, 249 (1902).
[29] G. JANDER und G. WINKLER *J. Inorg. Nucl. Chem.* **9**, 39 (1959).

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ACETAMID ALS NICHTWÄSSRIGES IONISIERENDES LÖSUNGSMITTEL—II

EMK-MESSUNGEN UND POTENTIOMETRISCHE TITRATIONEN IN GESCHMOLZENEM ACETAMID[1]

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Abstract—With a special type of molybdenum electrode ("gebremste Elektrode") acting like a hydrogen electrode reactions in molten acetamide analogous to neutralizations were followed by potentiometric titrations. An estimation of the ionic product of the pure solvent based on e.m.f.-measurements at 94°C gives a value $P = 3.2 \cdot 10^{-11}$. Both the e.m.f.-measurements and the potentiometric titrations prove the proposed mechanism of self-dissociation of the pure solvent.

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In einer vorausgegangenen Mitteilung[1] haben wir über das allgemeine Verhalten des geschmolzenen Acetamid als nichtwässriges ionisierendes Lösungsmittel, sowie über die konduktometrische Verfolgung von Neutralisationsreaktionen und Amphoterieerscheinungen berichtet. Die vorliegende Arbeit beschäftigt sich mit EMK-Messungen und potentiometrischen Titrationen, die weitere Aufschlüsse über das Verhalten des Acetamid als Lösungsmittel geben.

In dem protonenhaltigen Solvens Acetamid sollten unter Umständen die gleichen Elektrodenkombinationen zur Bestimmung der H^+-Konzentration verwendbar sein wie in Wasser (zur Vereinfachung der Schreibweise steht in allen Fällen $[H^+]$ an Stelle der Konzentration des solvatisierten Protons $[H^+ \cdot xCH_3CONH_2]$).

Es zeigte sich jedoch, dass dies aus zwei Gründen nicht möglich ist. Einmal lässt sich eine Wasserstoffelektrode nicht verwenden, da die platinierte Elektrodenoberfläche bei der Messtemperatur 94° nach kurzer Zeit inaktiv wird und infolgedessen die anfangs dem Logarithmus der H^+-Konzentrationsänderung proportionalen EMK-Werte rasch abfallen. Zum anderen sind die in Frage kommenden Vergleichselektroden in Acetamid unbrauchbar [vgl. dazu[2]]; Hg_2Cl_2 zersetzt sich in Acetamid unter Schwarzfärbung (Disproportionierung) und Silber/Silberhalogenidelektroden scheiden aus, weil die Silberhalogenide im alkalischen Gebiet unter Komplexbildung teilweise löslich sind.

Es wurde deshalb die Methode der gebremsten Elektrode mit praktisch verhinderter Diffusion nach MÜLLER[3] angewendet, bei der Indikator- und Vergleichselektrode aus dem gleichen Elektrodenmaterial bestehen und durch eine Kapillare getrennt sind. Im Raum der Vergleichselektrode (gebremsten Elektrode) kann also eine gegebene Anfangskonzentration über relativ lange Zeit aufrechterhalten werden, während im Raum der Indikatorelektrode durch Reagenszusatz die Konzentration des zu bestimmenden Ions, in diesem Falle die H^+-Konzentration, fortwährend verändert wird.

[1] 1. Mitt.: G. JANDER und G. WINKLER, *J. Inorg. Nucl. Chem.* **9**, 24 (1959).
[2] L. FISCHER, G. WINKLER und G. JANDER, *Z. Elektrochem.* **62**, 14 (1958).
[3] E. MÜLLER, *Z. Physik. Chem.* **135**, 102 (1928).

Als Elektrodenmaterial diente zunächst Gold, das wegen seiner schlechten Potentialeinstellung im alkalischen Gebiet durch Molybdän ersetzt wurde.

Molybdän spricht in geschmolzenem Acetamid genau wie in Wasser über den ganzen pH-Bereich konzentrationsrichtig auf die Änderung der H^+-Konzentration an (die Messgenauigkeit und die Geschwindigkeit der Potentialeinstellung sind im neutralen und sauren Gebiet besser als im alkalischen Gebiet).

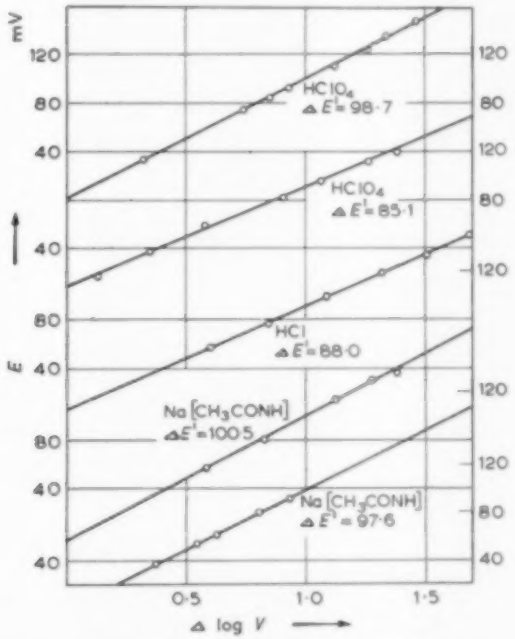

Abb. 1.—Lineare Abhängigkeit der EMK vom Logarithmus der Konzentration an Säuren- oder Basenanalogen.

In Abb. 1 wird die lineare Abhängigkeit der gemessenen EMK von dem Logarithmus der Konzentration an Säuren- oder Basenanalogen im Raum der Indikatorelektrode gezeigt (es ist aufgetragen auf der Ordinate E, auf der Abszisse $\Delta \log V$, d.h. der um die vorgegebene Anfangskonzentration korrigierte Logarithmus der Verdünnung).

Wie ersichtlich, ändert sich die Neigung der verschiedenen Geraden etwas von Messreihe zu Messreihe, d.h. die EMK-Änderungen für die Änderung der H^+-Konzentration um eine Zehnerpotenz schwanken um einen Mittelwert $\overline{\Delta E'} = 94{,}5$ mV (aus 11 Messreihen), mit einer maximalen Abweichung der einzelnen Messreihe von $\pm 20\%$. Diese Tatsache ist für analytische potentiometrische Säure-Basen-Titrationen ohne Belang, muss jedoch bei Absolutmessungen, wie bei der Abschätzung des Ionenproduktes von reinem Acetamid, beachtet werden.

Gemäss der Nernst'schen Gleichung müsste für die Messtemperatur 94° der Faktor $\Delta E' = (2{,}303RT)/(nF)$ gleich 72,8 mV sein. Da dies augenscheinlich nicht der Fall ist, muss der Wert $\Delta E'$ vor jeder Messung durch Eichung ermittelt werden.

Ein ähnliches Verhalten zeigen unbehandelte Mo- und W-Drähte in wässriger Lösung.[4]

Betreffs des Elektrodenmechanismus sei auf eine Untersuchung von EL WAKKAD und Mitarbeitern[5] über die W-Elektrode hingewiesen. Es geht daraus hervor, dass die Wasserstoffelektrodenwirkung auf einer Wechselwirkung zwischen den Redoxsystemen der verschiedenen Wolframoxyde unter Mitwirkung von Protonen beruht, wobei die Oxydschichten sehr fest haften und ausgesprochenen Isolatoreigenschaften besitzen, was die Konstanz der Eichkurve über längere Zeiträume erklärt.

Für die Mo-Elektrode in geschmolzenem Acetamid dürfte ein ähnlicher Mechanismus anzunehmen sein. Allerdings ist die Konstanz der Eichkurve über längere Zeiträume, wie aus Abb. 1 hervorgeht, vermutlich infolge der wesentlich höheren Messtemperatur im Vergleich zu den Messungen in wässriger Lösung etwas verschlechtert.

1. ABSCHÄTZUNG DER GRÖSSE DES IONENPRODUKTES VON REINEM ACETAMID

Eine EMK-Messung zwischen dem reinen Lösungsmittel im Raum der Vergleichselektrode und der Lösung einer starken Säure bekannten Gehaltes im Raum

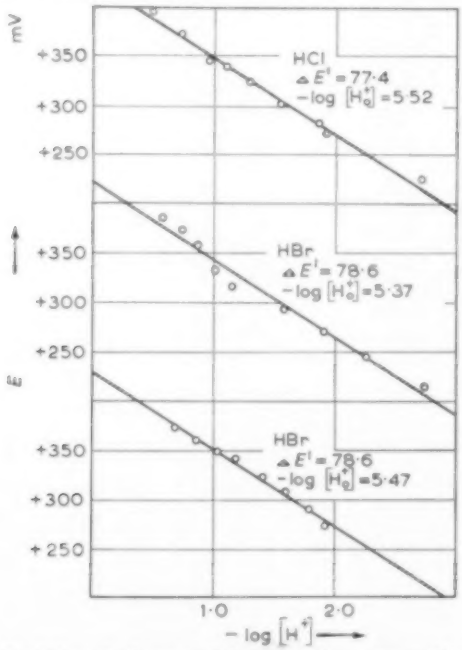

ABB. 2.—Ermittlung des Ionenproduktes von reinem Acetamid durch EMK-Messung.

der Indikatorelektrode gestattet nach Gleichung (1) die Ermittlung der H^+-Konzentration $[H_0^+]$ des reinen Lösungsmittels.

$$E = \Delta E' \cdot \log \frac{[H^+]}{[H_0^+]} \qquad (1)$$

[4] H. BRINTZINGER und B. ROST, *Z. Anal. Chem.* **120**, 161 (1940).
[5] E. S. EL WAKKAD, H. A. RIZK und J. G. EBAID, *J. Physik. Chem.* **59**, 1004 (1955).

Setzt man nach den Ergebnissen der Leitfähigkeitsmessungen[6] voraus, dass die zu den EMK-Messungen benutzten Säuren HCl und HBr vollständig dissoziiert sind ($HClO_4$ und HNO_3 wurden wegen evtl. oxydativer Einwirkung auf das Elektrodenmaterial nicht verwendet), kann man bei bekanntem $\Delta E'$ den Wert für $[H_0^+]$ berechnen.

Wegen der beträchtlichen Schwankungen in den $\Delta E'$-Werten wurden drei Messreihen mit HCl und HBr bei 94° durchgeführt, für welche die zugehörigen $\Delta E'$-Werte aus der jeweiligen Geraden graphisch entnommen wurden (Abb. 2; auf der Ordinate ist die gemessene EMK, auf der Abszisse der negative Logarithmus der H^+-Konzentration im Raum der Indikatorelektrode aufgetragen).

Für den negativen Logarithmus der H^+-Konzentration des reinen Lösungsmittels ergaben sich die Werte $-\log [H_0^+] = 5{,}52$, 5,37 und 5,47; das entspricht einem Ionenprodukt $P^{94} = [H^+]\cdot[CH_3CONH^-]$ von $0{,}9 \cdot 10^{-11}$, $1{,}8 \cdot 10^{-11}$ und $1{,}1 \cdot 10^{-11}$; Mittelwert der drei Bestimmungen $P = 1{,}3 \cdot 10^{-11}$.

Durch die Bestimmung der Eichkonstanten $\Delta E'$ für jede einzelne Messreihe wird zwar die Unsicherheit in dem Mittelwert $\overline{\Delta E'}$ ausgeschaltet, es bleiben aber zwei weitere mögliche Fehlerquellen, die nicht eliminiert werden können. Das ist einmal das an der Phasengrenzfläche zwischen den beiden verschieden konzentrierten Lösungen vorhandene Diffusionspotential und zum anderen die evtl. Veränderlichkeit des als konstant angesetzten "Nullpotentials" (vgl. Messmethodik). Aus diesem Grunde können die Werte für $-\log [H_0^+]$ nicht mit der Sicherheit bestimmt werden, die für eine angemessene Genauigkeit in P zu wünschen wäre. Der erhaltene Wert $P = 1{,}3 \cdot 10^{-11}$ bedeutet also lediglich eine grössenordnungsmässige Abschätzung der Eigendissoziation des geschmolzenen Acetamid.

2. POTENTIOMETRISCHE NEUTRALISATIONSTITRATIONEN

Zur Kontrolle der vorstehenden Ergebnisse wurden drei potentiometrische Säure-Basen-Titrationen bei 94° durchgeführt—$K[CH_3CONH]$ mit HBr, HCl mit $Na[CH_3CONH]$ und $K[CH_3CONH]$ mit HCl,—(Kurvenverlauf wie in Abb.3)—und daraus, wiederum nach Ermittlung der Eichkonstanten $\Delta E'$ aus der jeweiligen

TABELLE 1

Titration		c [Mol/kg]	$\Delta E'$ [mV]	ΔE [mV]	$P \cdot 10^{11}$
von	mit				
$K[CH_3CONH]$	HBr	0,075	103,6	676,3	3,0
HCl	$Na[CH_3CONH]$	0,092	99,9	647,8	3,3
$K[CH_3CONH]$	HCl	0,129	98,2	638,3	3,2
					Mittelwert: 3,2

Messung (wegen der grösseren Genauigkeit wurde $\Delta E'$ im sauren Teil der Titrationskurve bestimmt), für den Konzentrationsbereich 0,01 n sauer bis 0,01 n alkalisch aus der Höhe des Potentialsprunges ΔE das Ionenprodukt P bestimmt. Die Ergebnisse sind in Tabelle 1 zusammengefasst. Hinsichtlich der Genauigkeit der Bestimmung gilt natürlich auch in diesem Falle das vorstehend Gesagte.

[6] 3. Mitt.: G. JANDER und G. WINKLER, *J. Inorg. Nucl. Chem.* **9**, 39 (1959).

Es besteht also grössenordnungsmässig Übereinstimmung zwischen den beiden auf potentiometrischem Wege unabhängig voneinander bestimmten Werten des Ionenproduktes für das reine Acetamid. Es ist noch zu diskutieren, welchem der beiden Werte $P = 1{,}3 \cdot 10^{-11}$ bzw. $P = 3{,}2 \cdot 10^{-11}$ ein höherer Grad von Wahrscheinlichkeit zukommt. Da über den Charakter der "letzten Verunreinigungen" in reinstem Acetamid nichts ausgesagt werden kann und die Möglichkeit besteht, dass es sich um Verbindungen schwach sauren oder basischen Charakters handelt, erscheinen uns die nach der ersten Methode erhaltenen Werte unsicherer. Es ist deshalb der Wert aus den Säure-Basen-Titrationen $P = 3{,}2 \cdot 10^{-11}$ vorzuziehen, da in diesem Falle die geringe Konzentration der Verunreinigungen keine Rolle spielt.

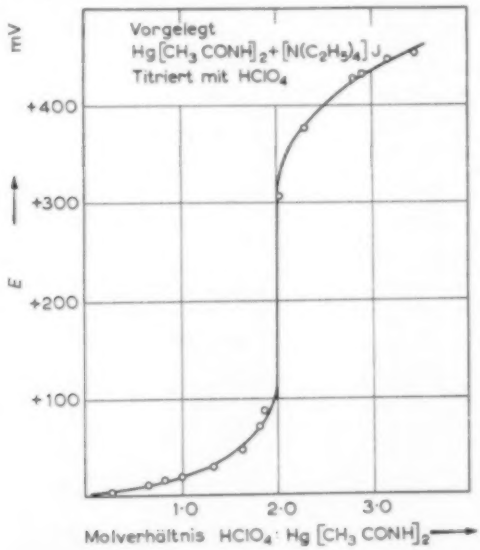

ABB. 3.—Potentiometrische Titration des durch doppelte Umsetzung aus $Hg[CH_3CONH]_2$ und $[N(C_2H_5)_4]J$ in Lösung erhaltenen Tetraäthylammoniumacetamid mit $HClO_4$.

$L\ddot{o}sungsmittel_{korr.}$	:	11,0 g
vorgelegt	:	61,8 mg Hg–Acetamid + 647 mg $[N(C_2H_5)_4]J$
äquiv. Menge	:	85,4 mg $2CH_3CONH_2 \cdot HClO_4$

Es soll an dieser Stelle noch darauf hingewiesen werden, dass man aus dem niedrigsten Wert der spezifischen Leitfähigkeit des reinen Acetamid ($\varkappa_0^{94}$ $2{,}6 \cdot 10^{-6}$) die maximale Grösse des Ionenproduktes abschätzen kann. Unter Voraussetzung der Gültigkeit des Kohlrausch-Gesetzes von der unabhängigen Ionenwanderung lässt sich aus den Grenzleitfähigkeiten geeignet ausgewählter starker Elektrolyte—im vorliegenden Fall wurden Pikrinsäure, Na-Pikrat und Na-Acetamid verwendet[16]—die hypothetische Grenzleitfähigkeit für vollständig dissoziiertes Acetamid berechnen [Gleichung (2)] und aus dem tatsächlich gemessenen $\varkappa_0$-Wert die Konzentration an dissoziiert vorliegendem Acetamid c_i nach Gleichung (3) bestimmen.

$$\Lambda_{[H^+][CH_3CONH^-]} = \Lambda_{HPi} + \Lambda_{Na[CH_3CONH]} - \Lambda_{NaPi} = 36{,}6_5 \tag{2}$$

$$c_i^{94} = \frac{1000 \cdot \varkappa_0}{\Lambda_{[H^+][CH_3CONH^-]}} = 7{,}1 \cdot 10^{-5} \tag{3}$$

Aus dem gefundenen c_i-Wert würde sich das Ionenprodukt zu $P^{94} = 5{,}0 \cdot 10^{-9}$ ergeben. Die Methode kann natürlich nur zur Abschätzung einer oberen Grenze des Ionenproduktes verwendet werden, da bei ihr vorausgesetzt ist, dass die Restleitfähigkeit nur durch die Eigendissoziation des Lösungsmittels hervorgerufen wird, was zweifelsohne nicht der Fall ist.

In Abb. 3 ist zur Ergänzung der konduktometrischen Titrationskurve[1] die potentiometrische Titration des durch doppelte Umsetzung aus $Hg[CH_3CONH]_2$ und $[N(C_2H_5)_4]J$ dargestellten Tetraäthylammoniumacetamid mit $HClO_4$ wiedergegeben. Die Form der Titrationskurve ist charakteristisch für alle potentiometrischen Säure-Basen-Titrationen in geschmolzenem Acetamid; die Potentialsprünge am Äquivalenzpunkt betragen zwischen 300 und 600 mV.

Ausser der potentiometrischen Titration starker Säuren mit starken Basen und umgekehrt lassen sich auch verschieden starke Säuren, deren Dissoziationskonstanten weit genug auseinander liegen, auf potentiometrischem Wege im Gemisch nebeneinander bestimmen. Abb. 4 zeigt als Beispiel die potentiometrische Titration eines

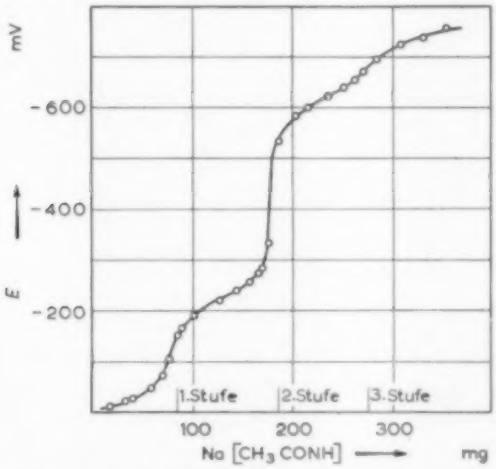

ABB. 4.—Potentiometrische Stufentitration verschieden starker Säuren mit Na-Acetamid.
vorgelegt: 208,5 mg $2CH_3CONH_2 \cdot HBr$ = 84,9 mg $Na[CH_3CONH]$
152,0 mg C_6H_5COOH = 101,2 mg $Na[CH_3CONH]$
111,5 mg $(CH_3CO)_2NH$ = 89,5 $Na[CH_3CONH]$
1. Stufe 84,9 mg $Na[CH_3CONH]$ 2. Stufe 186,1 mg $Na[CH_3CONH]$ 3. Stufe 275,6 mg $Na[CH_3CONH]$

Gemisches der starken Säure $2CH_3CONH_3 \cdot HBr$, der schwachen Benzoesäure und des als sehr schwache Säure fungierenden Diacetamid $(CH_3CO)_2NH$[7] mit $Na[CH_3CONH]$. Die beiden Potentialsprünge am Aquivalenzpunkt von HBr und Benzoesäure sind gut ausgebildet, während der letzte Potentialsprung infolge der starken Solvolyse des entstandenen Na-Diacetamid nur wenig ausgeprägt ist. Die Ergebnisse dieser EMK-Messungen und potentiometrischen Titrationen beweisen das für das geschmolzene Acetamid im Hinblick auf seine amphiprotischen Eigenschaften angenommene Eigendissoziationsschema.[1]

Es sei noch erwähnt, dass die für potentiometrische Titrationen verwendeten Alkaliacetamide[1] besonders rein sein müssen und keinesfalls infolge partieller Hydrolyse Alkaliacetat enthalten dürfen, da sonst zwei Potentialsprünge, einmal für die vorgelegte starke Säure und zum anderen für die aus dem verunreinigten Alkaliacetamid in Freiheit gesetzte Essigsäure, auftreten können (vgl. ähnliche Beobachtungen bei potentiometrischen Säure-Basen-Titrationen in Butanol[8]).

[7] B. GRÜTTNER, *Z. Anorg. Chem.* **270**, 223 (1952).
[8] L. A. WOOTEN und A. E. RÜHLE, *Analyt. Chem.* **6**, 449 (1934).

3. MESSMETHODIK

Die EMK-Messungen wurden bei 94,0° (Hoeppler-Ultrathermostat mit Glycerinfüllung; Gebr. Haake, Berlin) mit einem Philips-pH-Messgerät GM 4491 durchgeführt. Die Spannung wird bei diesem Gerät, auch ausserhalb des Kompensationsgleichgewichtes, völlig stromlos gemessen, d.h. es kann weder eine Elektrodenpolarisation noch eine Stromentnahme aus dem Normalelement ausserhalb des Kompensationsgleichgewichtes eintreten. Die Anzeige erfolgt trägheitslos mittels eines Elektronenstrahlindikators, der Messbereich erstreckt sich von 0–1415 mV, die Messgenauigkeit beträgt ± 1 mV $+ 0{,}2\%$ der gemessenen Spannung.

Die Angabe + oder — bezieht sich auf die Polarität der Indikatorelektrode gegenüber der Vergleichselektrode (gebremste Elektrode); die Vergleichselektrode ist über das Gerät geerdet.

Vor Beginn jeder Messung wird die Kapillare durch Öffnen des Quetschhahnverschlusses mit der Ausgangslösung bis zu einer bestimmten Eichmarke gefüllt und die im Raum der Indikatorelektrode befindliche Lösungsmenge um das entsprechende Kapillarvolumen korrigiert. Dann wird ca. 2 Stunden gewartet, bis sich das zwischen den beiden in die gleiche Lösung eintauchenden Elektroden vorhandene "Nullpotential", das wahrscheinlich durch Diffusionseffekte hervorgerufen wird, nicht mehr verändert. Das Nullpotential ist im allgemeinen von der Grössenordnung 5–40 mV, bei alkalischen Lösungen treten jedoch Potentialdifferenzen bis zu 200 mV auf. Unter der Voraussetzung, dass sich dieses Potential während der Messung nicht ändert, sind alle angegebenen Potentialwerte um das jeweils gemessene Nullpotential korrigiert.

Die verwendete Kapillare war so dimensioniert (Länge ~50 mm, Durchmesser 0,3 mm), dass ein Poteintialzusammenbruch infolge eines partiellen Konzentrationsausgleiches zwischen den beiden Elektrodenräumen durch Diffusion frühestens nach 8–10 Stunden eintrat.

Nach jeder Reagenszugabe wurde nach Umschütteln 20–30 Minuten bis zur konstanten Potentialeinstellung gewartet.

Die Darstellung der verwendeten säuren— und basenanalogen Verbinungen wurde bereits in der 1. Mitteilung beschrieben.[1]

Die Durchführung der vorliegenden Arbeit wurde durch Gewährung von ERP-Mitteln in grosszügiger Weise gefördert, wofür wir an dieser Stelle danken.

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ACETAMID ALS NICHTWÄSSRIGES IONISIERENDES LÖSUNGSMITTEL—III

LEITFÄHIGKEIT UND STÄRKE VON ELEKTROLYTEN IN GESCHMOLZENEM ACETAMID[1,2]

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(*Received* 24 *April* 1958)

Abstract—Measurements of the equivalent conductivity of salts or acid- and base-analogues in molten acetamide at 94°C showed complete dissociation of all salts with the exception of Zn-, Cd- and Hg^{II}-halides. Likewise strongly dissociated are the following acids and bases (in the order of increasing acidic or basic strength), whose relative strength was estimated by comparison with the "normal electrolyte" $N(C_2H_5)_4J$: *p*-toluenesulfonic acid, picric acid, HCl, HBr, HNO_3, $HClO_4$; Na-acetamide, K-acetamide. Thermodynamic dissociation constants of the weak acids 2,4-dinitrobenzoic acid, *o*-nitrobenzoic acid, salicylic acid, benzoic acid and the weak base piperidine were calculated from measurements of conductivity.

1. ÄQUIVALENTLEITFÄHIGKEIT VON SALZEN, SÄURENANALOGEN UND BASENANALOGEN VERBINDUNGEN

ALS bisher einzige Untersuchungen über die Leitfähigkeit von Neutralsalzen in geschmolzenem Acetamid liegen Messungen von WALKER und JOHNSON[3] bei 100° an Lösungen von KCl, KJ, KCN und $HgCl_2$ und von BELLADEN[4] bei 90° an Lösungen von KJ, NaCl, NaJ, $BaCl_2$ und $CaCl_2$ vor. Die von Belladen aus den Messwerten extrapolierten Grenzleitfähigkeiten bei unendlicher Verdünnung liegen für die 1-1-wertigen Elektrolyte in der Grössenordnung $\Lambda_0 \sim 39$–43.

Es besteht der Verdacht, dass die angegebenen Λ_0-Werte etwas zu hoch sind. Von Belladen werden keine Angaben über die benutzte Messzelle und Messanordnung, sowie über die zur Extrapolation der Λ_0-Werte verwendete Methode gemacht. Es wird lediglich angeführt, dass die Eichung mit einer n/50 KCl-Lösung vorgenommen wurde.

Im Rahmen der Untersuchung über Acetamid als ionisierendes Lösungsmittel wurden von uns die Äquivalentleitfähigkeiten von KJ, $[N(C_2H_5)_4]J$, der Na-Salze von Pikrin-, Benzoe-, Salicyl-, *o*-Nitrobenzoe- und 2.4-Dinitrobenzoesäure, von Piperidinhydrobromid, sowie von $HClO_4$, HNO_3, HBr, HCl, Pikrinsäure, *p*-Toluolsulfonsäure, K- und Na-Acetamid bei 94° in Abhängigkeit von der Konzentration gemessen.

Die erhaltenen Λ_c-Werte lassen sich nach der von SHEDLOVSKY[5] angegebenen

[1] 1. Mitt.: G. JANDER und G. WINKLER, *J. Inorg. Nucl. Chem.* **9**, 24 (1959).
[2] 2. Mitt.: G. JANDER und G. WINKLER, *J. Inorg. Nucl. Chem.* **9**, 32 (1959).
[3] J. W. WALKER und F. M. G. JOHNSON, *J. Chem. Soc.* **87**, 1597 (1905).
[4] L. BELLADEN, *Gazz. Chim. Ital.* **57**, 407 (1927).
[5] T. SHEDLOVSKY, *J. Amer. Chem. Soc.* **54**, 1411 (1932).

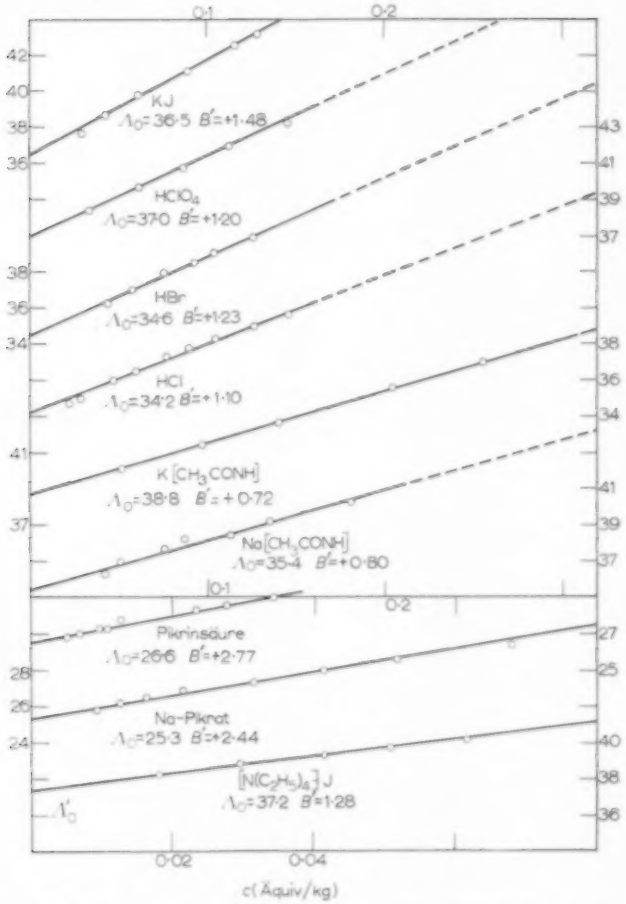

ABB 1.—Gültigkeit der Shedlovsky-Gleichung (1) für verschiedene Elektrolyte in geschmolzenem Acetamid.

erweiterten Form [Gleichung (1)] der Debye-Hückel-Onsager-Grenzgleichung für 1-1-wertige Elektrolyte wiedergeben (Abb. 1).

$$\frac{\Lambda_c + \beta\sqrt{c}}{1 - \alpha\sqrt{c}} \equiv \Lambda_0' = \Lambda_0 + Bc \qquad (1)$$

[wobei $\alpha = \dfrac{8{,}20 \cdot 10^5}{(\varepsilon T)^{3/2}}$, $\beta = \dfrac{82{,}5}{\eta\,(\varepsilon T)^{1/2}}$, $\varepsilon^{94} = 60,6$, $\eta^{94} = 0{,}0163$ Poise

(η^{94} aus den von DUNSTAN und MUSSEL[6] bei 105° und 120° gemessenen Viskositäten mit Hilfe dreier unabhängiger Gleichungen[7–9] auf 94° extrapoliert)].

[6] DUNSTAN und MUSSEL, *J. Chem. Soc.* **97**, 1935 (1910).
[7] BINGHAM, *Amer. Chem. J.* **43**, 287 (1910).
[8] LAUTIÉ, *Bull. Soc. Chim. Fr.* **7**, 690 (1940).
[9] STUART, *Petroleum* **10**, 74 (1947).

In Tabelle 1 sind die nach Gleichung (1) ausgewerteten Messergebnisse zusammengefasst [in Spalte 2 sind die durch Ausgleichsrechnung ermittelten Grenzleitfähigkeiten bei unendlicher Verdünnung (die Fehlerangabe bezieht sich auf den mittleren Fehler des Mittelwertes), in Spalte 3 der Zahlenwert der Konstanten B, in Spalte 4 der Zahlenwert der Konstanten $B' = B/\Lambda_0$ und in Spalte 5 der für die Ermittlung von B verwendete Konzentrationsbereich (c in Mol/kg) aufgeführt].

TABELLE 1

Verbindung	Λ_0	B	B'	Konz. Bereich
$[N(C_2H_5)_4]J$	37,24 ± 0,02	+47,6	+1,28	0,010–0,075
KJ	36,49 ± 0,08	+52,5	+1,48	0,025–0,13
Na-Pikrat	25,34 ± 0,05	+61,8	+2,44	0,009–0,05
$HClO_4$	37,00 ± 0,04	+44,2	+1,20	0,025–0,14
HNO_3	36,41 ± 0,02	+39,7	+1,09	0,03–0,10
HBr	34,59 ± 0,05	+42,4	+1,23	0,04–0,13
HCl	34,24 ± 0,06	+37,8	+1,10	0,02–0,15
Pikrinsäure	26,55 ± 0,03	+73,6	+2,77	0,005–0,035
p-Toluolsulfonsäure	23,73 ± 0,04	+53,9	+2,27	0,004–0,10
K-Acetamid	38,79 ± 0,04	+28,0	+0,72	0,05–0,25
Na-Acetamid	35,44 ± 0,10	+28,2	+0,80	0,04–0,18
Na-Benzoat	28,26 ± 0,04	+23,2	+0,82	0,008–0,10
Na-Salicylat	28,87 ± 0,07	+34,4	+1,19	0,004–0,14
Na-(*o*-Nitrobenzoat)	27,09 ± 0,01	+41,4	+1,53	0,01–0,06
Na-(2,4-Dinitrobenzoat)	25,63 ± 0,06	+55,6	+2,17	0,001–0,065
Piperidin-Hydrobromid	34,24 ± 0,06	+40,1	+1,17	0,01–0,10

Die als Solvate eingewogenen Verbindungen $2CH_3CONH_2 \cdot HClO_4$, $3CH_3CONH_2 \cdot HNO_3$, $2CH_3CONH_2 \cdot HBr$ und $2CH_3CONH_2 \cdot HCl$ wurden auf den Gehalt an HX umgerechnet und die eingewogene Lösungsmittelmenge um die bei jeder Einwaage neu hinzukommende Menge Kristall-Acetamid erhöht.

Die Tatsache, dass die Leitfähigkeitswerte aller untersuchten Verbindungen im Rahmen der Messgenauigkeit von ca. 1% der Gleichung (1) gehorchen, ist ein Beweis für die vollständige Dissoziation der gelösten Elektrolyte, denn die Gleichung (1) gilt nur für starke Elektrolyte, bei denen keine Assoziation vorliegt.

Der "nivellierende" Einfluss[10] des Lösungsmittels Acetamid lässt keine Absolutbestimmung des Stärkegrades der einzelnen Elektrolyte zu. Es kann lediglich eine Abschätzung des Stärkeverhältnisses in der Weise vorgenommen werden, dass man für verschiedene Konzentrationen die Werte des scheinbaren Dissoziationsgrades $\gamma' = \Lambda_c/\Lambda_0$ des "Normalelektrolyten" $[N(C_2H_5)_4]J$ mit den γ'-Werten der anderen Elektrolyte bei den entsprechenden Konzentrationen vergleicht. Daraus ergibt sich eine Reihe zunehmender Säurestärke *p*-Toluolsulfonsäure < Pikrinsäure < HCl < HBr < HNO_3 < $HClO_4$ bzw. zunehmender Basenstärke Na-Acetamid < K-Acetamid.

Hg-Acetamid ist eine extrem schwache Base, wie aus den konduktometrischen Titrationskurven[1] und den Leitfähigkeits absolutmessungen hervorgeht (Äquivalentleitfähigkeit bei 94°, c 0,1n, Λ_c 0,01).

[10] G. KORTÜM, *Lehrbuch der Elektrochemie* S. 223 (1957).

Schwach dissoziiert sind in Acetamid ferner die Halogenide von Zn, Cd und Hg^{II} (Äquivalentleitfähigkeiten bei 94°: ZnJ_2, 0,10 n, Λ_c 9,9; CdJ_2, 0,095 n, Λ_c 4,8; $HgBr_2$, 0,10 n, Λ_c 0,76; zum Vergleich KJ, 0,10 n, Λ_c 27,8].

Ein Vergleich der Λ_0-Werte von KJ und $[N(C_2H_5)_4]J$ in Acetamid mit den entsprechenden Werten in N-Methylacetamid,[11] N.N-Dimethylacetamid[12] und N.N-Dimethylformamid[13,14] auf der Grundlage der Walden'schen Regel $\Lambda_0\eta_0 = \Lambda_0'\eta_0' = \text{Const.}$ zeigt eine grössenordnungsmässige Übereinstimmung.

Da die Grösse des Walden'schen Produktes einen Hinweis auf Solvatationsänderungen gibt,[14,15] kann die gefundene geringe Erhöhung des Quotienten $\Lambda_{\text{N-Alkylamid}}/\Lambda_{\text{Acetamid}}$ gegenüber $\eta_{\text{Acetamid}}/\eta_{\text{N-Alkylamid}}$ als Beweis für eine etwas vergrösserte Solvatationsaffinität des Acetamid im Vergleich zu den alkylierten Amiden angesehen werden.

2. DISSOZIATIONSKONSTANTEN VERSCHIEDENER SCHWACHER SÄUREN UND BASEN IN ACETAMID

Für die schwachen Säuren 2,4-Dinitrobenzoesäure, *o*-Nitrobenzoesäure, Salicylsäure, Benzoesäure und die schwache Base Piperidin wurden von uns aus Leitfähigkeitsmessungen die thermodynamischen Dissoziationskonstanten K_0 in geschmolzenem Acetamid bei 94° nach der Methode von SHEDLOVSKY[16–18] bestimmt.

Die Λ_0-Werte für die schwachen Elektrolyte wurden unter Voraussetzung der Gültigkeit des Kohlrausch'schen Gesetzes von der unabhängigen Ionenwanderung aus $\Lambda_{HA} = \Lambda_{HPi} + \Lambda_{NaA} - \Lambda_{NaPi}$ bzw. $\Lambda_B = \Lambda_{[BH]Br} + \Lambda_{Na[CH_3CONH]} - \Lambda_{NaBr}$ ($\Lambda_{NaBr} = 33{,}3_8$) ermittelt.

In Abb. 2 wird die Gültigkeit der Shedlovsky'schen Beziehung für die vier schwachen Säuren durch graphische Darstellung von $1/\Lambda S(z)$ gegen $c\Lambda S(z)f^2$ gezeigt.

TABELLE 2

Verbindung	Λ_0	$K_0 \cdot 10^4$ bei 94°	pK-Wert in Acetamid	pK-Wert in Wasser
2,4-Dinitrobenzoesäure	26,8	11,9 ± 0,1	2,92	1,46
o-Nitrobenzoesäure	28,3	1,18 ± 0,01	3,93	2,19
Salicylsäure	30,1	1,91 ± 0,01	3,72	2,98
Benzoesäure	29,5	0,0217 ± 0,0002	5,66	4,20
Piperidin	36,3	0,00579 ± 0,00005	6,24	2,90

In Tabelle 2 sind die Werte der erhaltenen Dissoziationskonstanten den Werten in Wasser gegenübergestellt.

Die Unterschiede der pK-Werte in Acetamid und Wasser lassen sich dahingehend interpretieren, dass bei den Säuren ein Gegeneinanderwirken der beiden in Frage

[11] L. R. DAWSON, P. G. SEARS und R. H. GRAVES, *J. Amer. Chem. Soc.* **77**, 1986 (1955)
[12] G. R. LESTER, T. A. GOVER und P. G. SEARS, *J. Phys. Chem.* **60**, 1076 (1956).
[13] D. P. AMES und P. G. SEARS, *J. Phys. Chem.* **59**, 16 (1955).
[14] P. G. SEARS, E. D. WILHOIT und L. R. DAWSON, *J. Phys. Chem.* **59**, 373 (1955).
[15] V. S. GRIFFITHS und K. S. LAWRENCE, *J, Chem. Soc.* 473 (1956).
[16] T. SHEDLOVSKY, *J. Franklin Inst.* **225**, 739 (1938).
[17] R. M. FUOSS und T. SHEDLOVSKY, *J. Amer. Chem. Soc.* **71**, 1496 (1949).
[18] L. FISCHER, G. WINKLER und G. JANDER, *Z. Elektrochem.*. **62**, 4 (1958).

kommenden Einflüsse—etwas stärker basischer Charakter des Acetamid im Vergleich zu Wasser [Werte der Protonenaffinitäten bei BRIEGLEB[19,20]] und verringerte DK—stattfindet, während bei der Base Piperidin beide Einflüsse in gleicher Richtung,

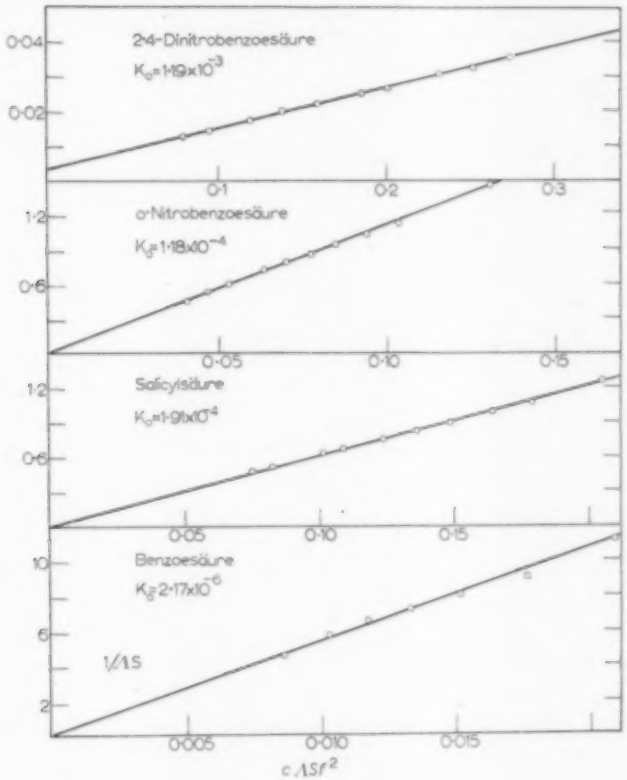

ABB. 2.

nämlich auf eine Verringerung der Dissoziation hin, wirksam sind. Da Protonenaffinität und DK beider Lösungsmittel von vergleichbarer Grössenordnung sind, ist zu erwarten, dass sich ausserdem Solvatationseffekte[21,22] stark bemerkbar machen werden, über die im Solvens Acetamid bisher noch keine Aussagen möglich sind.

3. MESSMETHODIK

Die Leitfähigkeitsmessungen wurden mit einer Philips-Leitfähigkeitsmessbrücke (Typ GM 4249) vorgenommen, die wahlweise mit einer Frequenz von 50 Hz oder 1000 Hz (Messspannung ca. 2 bzw. 3,5 Volt) gespeist werden kann und als Nullinstrument einen Elektronenstrahlindikator besitzt. Es wurde in Stellung "offene Brücke"—bei dieser Brückenschaltung können Widerstände mittels eines äusseren Vergleichswiderstandes gemessen werden—das Brückenverhältnis des Gerätes auf 1 : 1 eingestellt und der unbekannte Elektrolytwiderstand durch Vergleich mit einem

[19] G. BRIEGLEB, *Naturwissenschaften* **30**, 469 (1942).
[20] G. BRIEGLEB, *Z. Elektrochem.* **53**, 350 (1949).
[21] H. ULICH, *Z. Elektrochem.* **39**, 483 (1933).
[22] G. BRIEGLEB, *Naturwissenschaften* **30**, 436 (1942).

Präzisionswiderstand (Hersteller Fa. O. Wolff, Berlin; der Messbereich umfasst sieben Dekaden von 10^6 bis 10^{-1} Ohm, die Genauigkeit beträgt $\pm 0{,}01\,\%$) gemessen.

Zum Abgleich der kapazitiven Phasenverschiebungen, besonders bei geringeren Widerstandswerten, wurde parallel zum Vergleichswiderstand eine regelbare Kapazität von maximal 2400 pF geschaltet. Die beschriebene Anordnung gestattet in dem zu messenden Widerstandsbereich zwischen $3 \cdot 10^5$–$3 \cdot 10^2$ Ohm bei Verwendung von 1000 Hz als Messfrequenz die Einstellung scharfer Minima mit einer Genauigkeit von $\pm 0{,}1\,\%$, was für den vorliegenden Fall vollkommen ausreichend ist, da bei einem Fehler von $\pm 0{,}1\,\%$ in der Widerstandsmessung der Fehler in Λ_c fast ausschliesslich durch den Fehler der Einwaage bestimmt wird (eine Fehlerdiskussion ergab für den Fehler in Λ_c bei Einwaagen von weniger als 15 mg $> \pm 1{,}5\,\%$, bei Einwaagen zwischen 15 und 50 mg $\pm 1{,}5$-1, $0\,\%$ und bei Einwaagen über 50 mg ca. $\pm 0{,}8\,\%$).

Das verwendete Leitfähigkeitsgefäss hatte einen Volumeninhalt von ca. 25 ml und besass zwei Tauchelektroden aus Pt-Blech (Elektrodenoberfläche ca. 0,28 cm², Elektrodenabstand ca. 2,3 cm), deren Stromzuführungen räumlich so weit wie möglich getrennt und vollständig eingeschmolzen waren, so dass nur die Elektrodenbleche in die Lösung eintauchten; die Rückseite der Elektrodenbleche war mit Glas belegt. Zur Verringerung der Polarisation wurden die Elektroden platiniert. Sämliche Messungen wurden in einer N_2-Atmosphäre unter gelindem Überdruck durchgeführt, wodurch während der Messung bei geschlossenem Gefäss als auch bei Substanzzugabe das Eindringen von Luftfeuchtigkeit verhindert wurde. Die Substanzen wurden in fester Form aus Ampullen bzw. bei Flüssigkeiten aus einer Wägebürette zugegeben. Nach jeder Zugabe wurde durch mehrmaliges kräftiges Schütteln des Gefässes eine gute Durchmischung erzielt und nach Erreichen eines konstanten Widerstandswertes, im allgemeinen nach 20–30 Minuten, abgelesen. Das Leitfähigkeitsgefäss befand sich in einem Einsatz mit Paraffinöl, der in einem mit Glycerin gefüllten Hoeppler-Ultrathermostaten auf $94 \pm 0{,}05°$ gehalten wurde.

Die Eichung des Leitfähigkeitsgefässes erfolgte nach der von KORTÜM und WELLER[23] beschriebenen Methode. Im Konzentrationsbereich $3{,}8$–$3 \cdot 10^{-4}$ mol KCl ergab sich bei 18° mit Hilfe der Λ_c-Werte für KCl von FRAZER und HARTLEY[24] für die Zellkonstante $C_Z = 0{,}730 \pm 0{,}002$.

Für die Leitfähigkeitsmessungen wurde reinstes Acetamid mit einer spezifischen Leitfähigkeit $K_0^{94} = 2{,}6$–$3{,}5 \cdot 10^{-6}$ $\Omega^{-1}\,cm^{-1}$ verwendet; die angegebenen Λ_c-Werte sind um die jeweils gemessene Eigenleitfähigkeit korrigiert.

Die Reinigung des Acetamid sowie die Darstellung der zu den Messungen verwendendeten säurenanalogen und basenanalogen Verbindungen des Acetamid wurde bereits in der 1. Mitteilung beschrieben.[1]

Die Durchführung der vorliegenden Arbeit wurde durch Gewährung von ERP-Mitteln in grosszügiger Weise gefördert, wofür wir an dieser Stelle danken.

[23] G. KORTÜM und A. WELLER, *Z. Naturf.* **5a**, 451 (1950).
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THERMAL STABILITY OF SOME METAL SULPHATES*

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Abstract—The thermal decomposition of eleven (II) sulphates has been studied by a combination of thermogravimetric and differential thermal anlaysis. The relative decomposition temperatures are: $MnSO_4$ 755, $FeSO_4$ 537, $CoSO_4$ 708, $NiSO_4$ 675, $CuSO_4$ 598, $ZnSO_4$ 646, $CdSO_4$ 816, $PbSO_4$ 803, $MgSO_4$ 895, $CaSO_4$ 1149, and $SrSO_4$ 1374°C. Factors possibly influencing thermal stability of such salts are discussed, with special consideration of the effects of the metal's electronegativity and polarizing power on the condition of the anion.

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THE thermal stabilities of salts containing the same anion are well known to differ for different cations. For example, alkali metal salts such as sulphates, carbonates, nitrates and perchlorates possess greater stability than the corresponding salts of less reactive metals, or the corresponding free acids. Thermal decomposition of such compounds may well be a very complex process. The temperature at which its rate first becomes perceptible may depend on the atomic structure of the metal, the extent to which the metal atoms are cationic in the compound, their radius and polarizing power, the crystal structure of the salt and of its solid decomposition products, the extent to which the complex negative group is truly anionic, its radius and polarizability, the mechanism of the decomposition, the nature of the products both intermediate and final, the diffusion of volatile products through the crystal, and perhaps other factors. Despite this potentiality for complexity, one can recognize in the published data a remarkably consistent tendency toward greater stability, the lower the electronegativity of the metal and the larger its crystal radius.

This tendency suggests that a complex anion may have greatest stability when (1) it has most complete control of the valence electrons, and (2) it exists in an environment of lowest polarizing power. The electronegativity of the metal would determine the extent to which the anion could control the valence electrons, and the lower this electronegativity, the more complete the control. The polarizing power of the metal atom, determined fundamentally by its structure and positive charge, would diminish with increasing radius. The effect of radius when electronegativity effects may be assumed equal is illustrated by the greater stability of KBH_4 than $NaBH_4$.[1]

It is therefore of interest to discover whether an approximately quantitative relationship among decomposition temperature, metal electronegativity, and crystal radius of the metal atom can be established. Then for any given compound, agreement with such a relationship would imply that contributions by the other factors mentioned above are relatively insignificant, and would provide a useful insight into the nature of such compounds, helping toward a practical understanding of their relative stabilities.

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[1] A. G. OSTROFF and R. T. SANDERSON, *J. Inorg. Nucl. Chem.* **4**, 230 (1957).

To investigate this possibility, it was necessary first to choose a series of similar salts of a common anion and determine on a strictly comparable basis, the temperatures of thermal decomposition, Anhydrous sulphates were selected as being most

TABLE 1.—DECOMPOSITION TEMPERATURES OF SOME METAL SULPHATES[a] (°C)

Sulphate	This work	Other investigators	Observed intermediate product	Final non-volatile product
$MnSO_4$	755	820[a(2)], 924[a(3)], 1030[d(4)], 699[d(5)]		Mn_3O_4
$FeSO_4$	537	251[a(6)], 360[a(7)], 470[c(8)], 167[d(5)]		Fe_2O_3
$CoSO_4$	708	720[a(2)], 904[ab(3)], 880[bc(4)], 350[e(9)]		Co_3O_4
$NiSO_4$	675	700[a(2)], 848[ab(3)], 600[d(4)]		NiO
$CuSO_4$	598	845[bc(4)], 341[d(10)], 600[e(11)], 620[e(12)]	$2CuO{\cdot}SO_3$	CuO
$ZnSO_4$	646	670[ab(12)], 846[ab(3)], 702[d(5)], 610[e(13)]	$3ZnO{\cdot}2SO_3$	ZnO
$CdSO_4$	816	780[a(2)], 827[d(5)], 900[e(11)], 820[e(12)]		CdO
$PbSO_4$	803	637[d(5)], 860[e(14)]		PbO
$MgSO_4$	895	880[a(15)], 890[d(5)], 860[e(16)]		MgO
$CaSO_4$	1149	1000[e(17)], 1200[d(5)]		CaO
$SrSO_4$	1374	1200[e(18)], 1600[f(19)]		SrO

[a] $CaSO_4$ and $SrSO_4$ were studied over the range 25–1590°. The other sulphates were studied over the range 25–1025°.

[a] Determined in a vacuum. [b] Decomposition temperature when equilibrium pressure of gaseous decomposition products is one atmosphere. [c] Heated in a tube closed at one end with a current of air. [d] Heated in a current of dry air. [e] Heated on a thermobalance. [f] Studied by DTA.

readily obtainable for a sufficiently large number of elements. To simplify the problem, only sulphates of the general formula, MSO_4, were studied. Although detailed structural analyses have not been reported for all these sulphates, X-ray powder diagrams indicate that they are similar in crystal structure.

All these sulphates have been studied previously by others, but unfortunately, widely discrepant values are reported for the same compounds, making impossible any dependable correlation. Therefore we have measured anew the thermal decomposition temperatures and studied the nature of the decompositions, by thermogravimetric and differential thermal analysis. The results, with comparisons of previous data, are summarized in Table 1. Differences between temperatures reported

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[18] N. UNOHARA, *J. Chem. Soc. Japan* **74**, 998 (1953).
[19] S. D. SHARGORODSKII, *Ukrain. Khim. Zh.* **15**, 332 (1949).

previously and herein are to be ascribed chiefly to differences in experimental procedure and definition.

The problem of determining meaningful decomposition temperatures is complicated by the gradual way in which the rate of decomposition may increase from zero, with increasing temperature. We have defined the decomposition temperature as the temperature at which the recorded weight curve first breaks detectably from constancy under carefully standardized operation of the thermobalance (as described in the following section). Such a definition seems quite satisfactory if the chief significance of the data is, as in this work, to permit an accurate comparison of the *relative* stabilities of different sulphates. Reproducibility within a range of three or four degrees was readily obtained. Each of the new decomposition temperatures reported in Table 1 is the average of several separate determinations.

The question of whether such seemingly arbitrary decomposition temperatures are acceptable as *absolute* values required further study. To investigate this question, we first determined the decomposition temperature by the standard procedure. We then repeated the experiment, slowing the heating rate greatly, at temperatures a few degrees below the observed decomposition temperature, to study the progress of decomposition over a much longer period of time. It was observed that at temperatures slightly below the observed "decomposition temperature." the rate of decomposition was extremely low, less than 0·1 per cent in 15 min, compared to about 0·6 per cent in 15 min at the "decomposition temperature" or slightly above. Therefore, although an absolute decomposition temperature cannot be precisely defined, the relative values obtained seem reasonably close to representing it.

It should be emphasized that, as implied at the beginning of this paper, we were at no time studying systems at equilibrium, and it is doubtful if in most cases equilibrium conditions could be achieved. Furthermore, as indicated in Table 1, the mode and/or products of decomposition were seldom if ever directly comparable. Unfortunately, the only possible consistent observation that can be made is that all sulphates are thermally unstable, and when decomposition begins, part of the products are volatile and weight loss results.

EXPERIMENTAL DETAILS

The preparation and analysis of the anhydrous sulphates studied are indicated in Table 2.

The differential thermal analysis and thermogravimetric analysis (DTA-TGA) apparatus consisted of a means of weighing automatically a sample suspended in a furnace and simultaneously observing any thermal changes therein as the temperature of the sample was changed at a constant rate. The weight changes and thermal effects were indicated as a function of temperature and time on the same chart by means of a multipoint recorder. In this way it was possible to correlate weight changes with changes in heat content simply and directly as a function of temperature.

The construction of the automatic thermobalance including the circuits for maintaining continuous balance and for making a continuous record of the weight has been described by MAUER.[26] The most significant changes in the apparatus used in these experiments were the replacement of the analytical balance used by MAUER with a semi-micro balance, and the concomitant changes in the rest of the system to permit precise operation with smaller samples.

[20] P. DUBOIS, *C.R. Acad. Sci., Paris* **198,** 1502 (1934).
[21] J. KENDALL and A. W. DAVIDSON, *J. Amer. Chem. Soc.* **43,** 979 (1921).
[22] T. E. THORPE and J. I. WATTS, *J. Chem. Soc.* **37,** 112 (1880).
[23] J. N. FRIEND, *Textbook of Inorganic Chemistry* Vol. IV, p. 35. Griffin, London (1931).
[24] R. E. BARIEAU and W. F. GIAUQUE, *J. Amer. Chem. Soc.* **72,** 5676 (1950).
[25] L. F. AUDRIETH (Editor), *Inorganic Synthesis* Vol. III, p. 19. McGraw-Hill, New York (1950).
[26] F. A. MAUER, *Rev. Sci. Instrum.* **25,** 598 (1954).

The differential thermal analysis method was similar to that described previously.[27] The differential thermocouple and the thermocouple indicating the furnace temperature were platinum–platinum-10% rhodium, calibrated at several fixed points. The output of this differential couple was fed into a high gain D.C. amplifier and thence through a matching filter network to the multipoint recorder.

The sample for continuous gravimetric analysis was contained in a thin platinum bucket suspended in the furnace environment by means of a long platinum wire extending from the left arm of a semi-micro balance. The differential thermal analysis samples were contained in two very thin (0·0005 in. thick) platinum containers 7/32 in. in diameter and 3/8 in. high, possessing re-entrant wells to receive the terminals of the differential thermocouple. The furnace environment consisted of concentric

TABLE 2.—PREPARATION AND ANALYSIS OF ANHYDROUS SULPHATES

Compound	Preparation*	Ref.	Metal		Sulphate	
			Anal.	Theory	Anal.	Theory
$MnSO_4$	$MnSO_4 \cdot H_2O$, 8 hr at 550° in N_2	20	36·86	36·38	65·54	63·62
$FeSO_4$	$FeSO_4 \cdot 7H_2O$, slowly to 290° in H_2	21	36·74	36·75	63·37	63·27
$CoSO_4$	$CoSO_4 \cdot 7H_2O$, 4 hr at 270° in N_2	22	38·17	38·02	62·26	61·98
$NiSO_4$	$NiSO_4 \cdot 6H_2O$, 4 hr at 370° in air	23	37·78	37·92	62·19	62·08
$CuSO_4$	$CuSO_4 \cdot 5H_2O$, 5 hr at 260° in N_2		39·44	39·80	60·05	60·17
$ZnSO_4$	$ZnSO_4 \cdot 7H_2O$, 5 hr at 340° in N_2	24	40·72	40·50	59·54	59·50
$CdSO_4$	$CdSO_4 \cdot 8/3H_2O$, 4 hr at 270° in N_2		54·85	53·92	46·20	46·08
$PbSO_4$	H_2SO_4 added to $Pb(C_2H_3O_2)_2$		68·42	68·32	31·60	31·68
$MgSO_4$	$MgSO_4 \cdot 7H_2O$, 3 hr at 340 in N_2		20·04	20·20	78·86	79·80
$CaSO_4$	$CaSO_4 \cdot 2H_2O$, 3 days at 200° in air		29·50	29·44	69·31	70·56
$SrSO_4$	H_2SO_4 added to $Sr(NO_3)_2$	25	48·12	47·70		

* All chemicals used were Mallinckrodt Analytical Grade.

silica or alumina tubes which permitted the active and reference samples to be kept at the same temperature in the furnace while providing a controlled atmosphere for the reaction system. The inner tube was permanently fixed about the wire leading to the balance and was partially cut away around the three sample containers. The outer tube was removable to permit easy access to the sample containers thus facilitating loading. The dimensions of this apparatus are not critical and may be adjusted within wide limits to accommodate various sample sizes and furnace dimensions. It is important only that the three samples be in a uniform temperature field.

The furnace consisted of a well insulated alundum core heated by means of a Kanthal winding. For temperatures in excess of 1200° the alundum reaction vessel itself was heated by a platinum winding made directly on the tube inside the Kanthal wound core. Both windings were bifilar to reduce inductance in the differential thermocouples. It was possible by means of this furnace to study samples at temperatures as high as 1600°.

In operation the atmosphere surrounding the active samples and the reference sample could be carefully controlled, by passing any desirable gas or gas mixture through the apparatus. In all these runs, nitrogen gas flowed through the apparatus at a sufficient rate (84 ml/mm) to prevent back diffusion of oxygen from the air. This flow of gas swept the volatile decomposition products rapidly and completely into the outside atmosphere. The temperature environment of the sample was governed by a programme controller capable of conducting any reasonable temperature increase or decrease at a constant rate. In the runs described herein, which were observed on the heating cycle only, the usual rate of temperature rise was 9°C/min. Much lower rates of temperature rise were used, after preliminary runs, to verify and examine further the precise temperatures at which these substances began to lose weight.

[27] E. D. GUTH, J. R. HOLDEN, N. C. BAENZIGER and L. EYRING, *J. Amer. Chem. Soc.* **76**, 5239 (1954).

DISCUSSION

The electronegativities of the transition metals are not yet determinable by the "stability ratio" method,[28,29] but values from thermal data have been reported by HAISSINSKY,[30] who considers the electronegativity to vary with valence.

He gives, on the Pauling scale, Cr(II) 1·5, Mn(II) 1·4, Fe(II) 1·65, Co(II) 1·7, and Ni(II) 1·7. Although Mn(II) is unique in its half-filled 3*d* orbitals, a value of about 1·6 would seem more reasonable for its electronegativity. Both values are considered in the following discussion. Electronegativities of the other metals are "SR" values.[28]

In accordance with the preceding speculation concerning the possible effects of

TABLE 3.—METAL ELECTRONEGATIVITIES AND EMPIRICAL CRYSTAL RADII

Metal	S	r (Å)	$(r/S)^{\frac{1}{2}}$
Mn	2·0	0·91	0·67
	2·4		0·62
Fe	2·6	0·83	0·57
Co	2·6	0·82	0·57
Ni	2·8	0·78	0·53
Cu	2·43		
Zn	2·84	0·83	0·54
Mg	1·56	0·78	0·71
Ca	1·22	1·06	0·93
Sr	1·10	1·27	1·07
Cd	2·59	1·03	0·63
Pb	3·08	1·32	0·65

polarization and electronegativity, we have sought to express the sulphate decomposition temperature T(°K) as a function of r/S, where S is the electronegativity expressed as "stability ratio",[29] and r is the empirical crystal radius[31] of the metal atom. These values are given in Table 3. Although a number of alternative forms are possible, the following linear relationship is found convenient:

$$T = 1286\,(r/S)^{\frac{1}{2}} + 247 \qquad (1)$$

This is shown graphically in Fig. 1. It may be observed that an electronegativity of 1·6 gives closer conformity of $MnSO_4$, and that $FeSO_4$ is completely anomalous. Perhaps the great tendency of Fe(II) to become Fe(III) in the crystal lends greater significance in $FeSO_4$ to the factors neglected in equation (1) than is true for any of the other metal sulphates studied here.

Certainly the data are not considered adequate to establish an exact fundamental relationship. They are interesting, however, because they suggest that a reasonable and simple approach to this complex problem can help toward a practical understanding. One can see, for example, that the encasement of a cation in ligands such as

[28] R. T. SANDERSON, *J. Chem. Educ.* **32**, 140 (1955).
[29] R. T. SANDERSON, *J. Chem. Phys.* **23**, 2467 (1955).
[30] M. HAISSINSKY, *J. Phys. Radium* **7**, 7 (1946).
[31] V. M. GOLDSCHMIDT, *Geochemische Verteilungsgestze der Elemente*. Skrifter det Norske Videnskaps-Akad. Oslo I. Matem.—Naturvid Klasse (1926).

water molecules would have the double effect of ensuring more complete control of the valence electrons by the anion, and shielding the anion from polarization by the cation. The fact that many more hydrated than anhydrous complex salts are known is consistent with this reasoning. Similarly, the relative instability of the free acids is

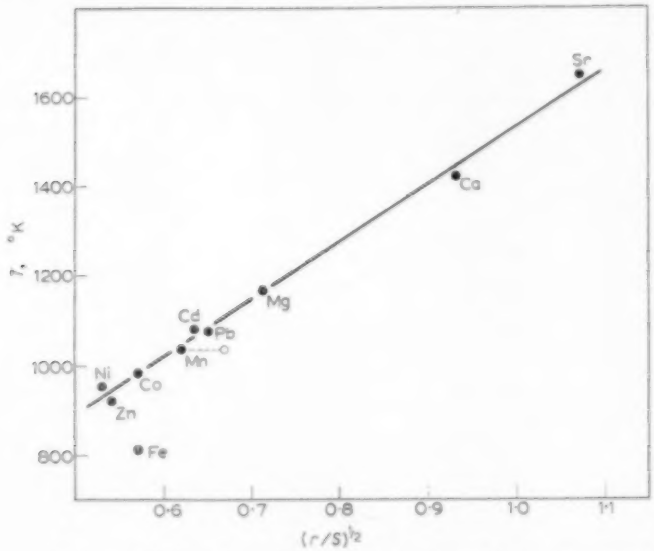

Fig. 1.—Relation of metal radius and electronegativity to decomposition temperature of some (II) sulfates.

understandable in view of the relatively high electronegativity and high polarizing power of the hydrogen. Very few data in the literature on (I) and (III) sulphates and on carbonates, nitrates, etc., are adequate for exact quantitative comparisons, but they do indicate at least approximate consistency with the results of this work on (II) sulphates.

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THE REACTION OF DIBORANE WITH BORON TRICHLORIDE IN THE PRESENCE OF ETHERS—THE CHLOROBORANE ETHERATES*†

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Abstract—Diborane does not react to any significant extent with boron trichloride in the absence of ethers. In the presence of ethers (dimethyl ether, diethyl ether, diglyme, tetrahydrofuran and tetrahydropyran) reaction readily occurs at room temperatures to form chloroborane etherates, as indicated by the equations:

$$B_2H_6 + BCl_3 + 3R_2O \rightarrow 3H_2ClB{\cdot}OR_2$$
$$B_2H_6 + 4BCl_3 + 6R_2O \rightarrow 6HCl_2B{\cdot}OR_2$$

These chloroborane etherates may also be synthesized from the alkali metal borohydrides in accordance with the reactions:

$$MBH_4 + BCl_3 + 2R_2O \rightarrow 2H_2ClB{\cdot}OR_2 + NaCl$$
$$MBH_4 + 3BCl_3 + 4R_2O \rightarrow 4HCl_2B{\cdot}OR_2 + NaCl$$

Their formation accounts for the low yield of diborane realized in treating the alkali metal borohydrides with an excess of boron trichloride in ether solutions. A number of the chloroborane etherates have been isolated and characterized. They react with olefins to form organoborane derivatives and to reduce the carbonyl groups in typical ketones, but not in esters.

IN examining the formation of diborane by treatment of sodium borohydride with boron trifluoride and boron trichloride, we observed an interesting difference in the behaviour of these two compounds.[1] An excess of boron trifluoride did not affect the essentially quantitative yield of diborane, whereas an excess of boron trichloride resulted in marked decreases in the amount of diborane evolved from the reaction mixture. Only by the use of the precise stoicheiometric quantity of boron trichloride was it possible to realize the maximum yield of diborane.

It was apparent that the results could be accounted for if the diborane and excess boron trichloride reacted to form non-volatile products, chloro derivatives of diborane. Indeed, in the electric discharge procedure for the synthesis of diborane, the reaction product obtained by passing hydrogen and boron chloride through the discharge apparently consists of a mixture of boron trichloride and partially hydrogenated material.[2] However, these materials are unstable, and readily disproportionate into boron trichloride and diborane. It was only by applying great experimental skill, that BURG was able to isolate and characterize monochlorodiborane,

* Molecular Addition Compounds. II.

† Based upon a thesis submitted by P. A. TIERNEY in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

‡ Standard Oil Research Foundation Fellow, 1955–1956. Parke, Davis and Company Fellow, 1956–1957.

[1] H. C. BROWN and P. A. TIERNEY, *J. Amer. Chem. Soc.* **80**, 1552 (1958).
[2] H. I. SCHLESINGER and A. B. BURG, *J. Amer. Chem. Soc.* **53**, 4321 (1931).

B_2H_5Cl, as one of the disproportionation products. Within a short time at room temperature this material was transformed into diborane and boron trichloride.[3]

In spite of the reported instability of the chloroboranes, it appeared that they might be stabilized by the ethers used as reaction media. Accordingly, a study was undertaken of the reaction of diborane with boron trichloride in the presence of several representative ethers.

RESULTS

Equimolar mixtures of diborane with boron trichloride or with boron trifluoride at room temperature exhibited pressures which were additive for the two components, and these pressures exhibited no significant change over 24 hr. No evidence of any reaction was observed. Diborane was no more soluble in a dilute solution of boron trifluoride in diglyme than in the solvent itself. On the other hand, diborane was rapidly absorbed by a dilute solution of boron trichloride in diglyme (diethyleneglycol dimethyl ether). One mole of diborane reacted per mole of boron trichloride present.

Solutions of boron trichloride in diglyme are relatively unstable—the ether is split with the formation of methyl chloride.[1] However, such solutions saturated with diborane appeared to be stable over long periods of time.

Because the low volatility and polyfunctionality of diglyme introduced experimental and interpretive difficulties, the phenomenon was examined with other simpler ethers, such as dimethyl ether, diethyl ether, tetrahydrofuran and tetrahydropyran. Diethyl ether and tetrahydropyran were the preferred reactants because of their demonstrated stability toward splitting by boron trichloride.[1]

An equimolar mixture of boron trichloride and diborane was treated with an excess of diethyl ether at 0°. Small increments of the ether were removed at 0° until the pressure dropped sharply to 3 mm and remained sensibly constant at this value. The molar ratio of ether to boron trichloride was 3·0. The product was a liquid which melted over a wide range, −85 to −105°.

In the case of tetrahydropyran, the corresponding reaction product, formed by mixing equimolar amounts of diborane and boron trichloride with three molar equivalents of the ether, appeared to be more stable, melting sharply at 19–20°. Tetrahydrofuran formed a similar derivative, m.p. −36° to −38°.

An experiment was carried out in a sealed tube with a 3 : 1 molar mixture of dimethyl ether and boron trichloride and an excess of diborane. After 36 hr at room temperature, the excess diborane was recovered by distillation from the reaction mixture at −78°. The results indicated that precisely one mole of diborane had reacted per mole of boron trichloride present. The melting point of the product was −20 to −21°.

These results clearly indicate that boron trichloride and diborane do not react significantly in the absence of ethers, but in their presence undergo reaction to form liquid products of low volatility, containing boron, active hydrogen, chloride, and ether in the ratio 1 : 2 : 1 : 1. On this basis the reactions can be written:

$$B_2H_6 + BCl_3 + 3(CH_3)_2O \rightarrow 3BH_2Cl{\cdot}O(CH_3)_2$$
$$B_2H_6 + BCl_3 + 3(C_2H_5)_2O \rightarrow 3BH_2Cl{\cdot}O(C_2H_5)_2$$
$$B_2H_6 + BCl_3 + 3(CH_2)_4O \rightarrow 3BH_2Cl{\cdot}O(CH_2)_4$$
$$B_2H_6 + BCl_3 + 3(CH_2)_5O \rightarrow 3BH_2Cl{\cdot}O(CH_2)_5$$

[3] A. B. BURG, *J. Amer. Chem. Soc.* **56**, 499 (1934).

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It was also observed that boron trichloride and diborane in a 4 : 1 molar ratio reacted with ethyl ether to form relatively stable, non-volatile products. Ether was removed at 0° from a reaction product of this composition in excess ether until the pressure dropped suddenly to a value near zero. At this point the ratio of ether to boron trichloride was 1·5. A similar experiment was carried out with tetrahydropyran. The observed ratios of reactants corresponds to the possible formation of a dichloroborane etherate and tetrahydropyranate:

$$B_2H_6 + 4BCl_3 + 6(C_2H_5)_2O \rightarrow 6BHCl_2{\cdot}O(C_2H_5)_2$$

$$B_2H_6 + 4BCl_3 + 6(CH_2)_5O \rightarrow 6BHCl_2{\cdot}O(CH_2)_5$$

The ethyl ether product exhibited a melting point of −25 to −30°, whereas the tetrahydropyran derivative melted at 10–15°.

In the case of the monochloroborane etherates, the stoicheiometry of the reaction clearly establishes the formation of the product with the composition, $BH_2Cl{\cdot}OR_2$. In the case of the dichloroborane etherates, the stoicheiometry alone cannot eliminate the possibility that the reaction product consists of a mixture of the known boron trichloride etherates[4–6] and the corresponding monochloroborane etherates.

$$B_2H_6 + 4BCl_3 + 6R_2O \rightarrow BH_2Cl{\cdot}OR_2 + BCl_3{\cdot}OR_2$$

Diethyl ether–boron trichloride melts at 56°. The low melting point, −25 to −30°, of the "dichloroborane etherate" suggests that large quantities of the trichloride addition compound, required by the above equation (50 mole per cent), cannot be present in the reaction product. It is possible that the reaction product consists primarily of the $BHCl_2{\cdot}OR_2$ product with minor equilibrium quantities of the $BH_2Cl{\cdot}OR_2$ and $BCl_3{\cdot}OR_2$ derivatives present. This would account for the relatively wide range observed for the melting points. A more detailed study of these products has been undertaken to resolve these questions.*

A solution of sodium borohydride in diglyme was treated with an equimolar quantity of boron trichloride. No diborane was evolved. The supernatant solution was separated from the precipitate, presumably sodium chloride, and analysed for boron, chloride and active hydrogen. The analysis corresponded to the formation of the monochloroborane etherate. The chemical behaviour of the solution corresponded precisely to the product obtained by the reaction of diborane with boron chloride in diglyme. Consequently, the reaction may be written:

$$NaBH_4 + BCl_3{\cdot}OR_2 + OR_2 \rightarrow NaCl\downarrow + 2BH_2Cl{\cdot}OR_2$$

The utility of the chloroborane etherates as hydrogenation and hydroboration reagents was briefly examined. At room temperature chloroborane ethyl etherate rapidly reduced acetone and related ketones, but did not affect esters, such as ethyl acetate. Ethylene reacted with dichloroborane pyranate at room temperature to form an organoborane, presumably triethylboron, and tetrahydropyran–boron trichloride.

* Research in progress with Mr. G. KLENDER.

[4] E. WIBERG and W. SUTTERLIN, *Z. Anorg. Chem.* **202,** 22 (1931) report the melting point of dimethyl ether–boron trichloride to be 76°.

[5] W. NESPITAL, *Z. Phys. Chem.* **B 16,** 153 (1932) reports the melting point of diethyl ether–boron trichloride to be 56°.

[6] J. GRIMLEY and A. K. HOLLIDAY, *J Chem. Soc.* 1212 (1954) report the melting points of tetrahydrofuran–boron trichloride as 38–52°, and tetrahydropyran–boron trichloride as 49–52°.

DISCUSSION

It is quite evident from the results that there is a remarkable difference in the behaviour of boron trifluoride and boron trichloride toward diborane in the presence of ethers. The rapid reaction of boron trichloride with diborane in the presence of ethers to form the relatively stable, non-volatile products, the monochloroborane and dichloroborane etherates, accounts for the deletorious effect of excess boron trichloride in the generation of diborane from alkali metal borohydrides.[1]

The marked difference in the behaviour of boron trichloride and boron trifluoride in these reactions may be attributed to the greater effect of chlorine over fluorine on the acid strength of boron acids.[7] On this basis both $BHCl_2$ and BH_2Cl would be sufficiently strong acids to form stable addition compounds with ethers, whereas the corresponding fluorine derivatives, BHF_2 and BH_2F, would be less strong acids and would result in less stable derivatives. Consequently the driving force for the reaction would come primarily from the replacement of one stable co-ordination bond by three, individually weaker, but collectively stronger, co-ordination bonds.

$$B_2H_6 + Cl_3B{\cdot}OR_2 + 2R_2O \rightarrow 3BH_2Cl{\cdot}OR_2$$

The chloroborane etherates exhibit many of the hydrogenation and hydroboration reactions of diborane itself. Moreover, the complexes are liquids which can be handled more readily than gaseous diborane. Consequently, they may prove to be useful reagents for organic syntheses and we are currently examining their potentialities for this purpose.*

EXPERIMENTAL

Apparatus. Except where otherwise stated, all experiments were conducted in the usual all-glass high vacuum system in which the materials came in contact only with glass and mercury.[8]

Analyses. Active hydrogen was measured by hydrolysing samples in a water-filled inverted burette. Chloride was determined as hydrochloric acid by titration with standard sodium hydroxide using methyl red as indicator, following hydrolysis in a closed system. Boron was determined as boric acid by adding mannitol and titrating with standard sodium hydroxide using phenolphthalein as indicator.

Materials. Boron trichloride (Matheson), v.p. 481 mm at 0°, was purified through the formation and dissociation of its nitrobenzene addition compound.[7] Diborane was prepared from sodium borohydride.[1]

Diglyme (Ansul Chemical Company) was twice distilled from lithium aluminium hydride under reduced pressure: b.p. 64° at 16 mm, n_D^{20} 1·4087. Tetrahydropyran (Dupont), after 24 hr over calcium hydride, was twice distilled from lithium aluminium hydride under nitrogen: b.p. 86–87° at 742 mm: n_D^{20} 1·4203; v.p. 75 mm at 28°, 20 mm at 0°. Tetrahydrofuran was treated with sodium hydroxide pellets and then twice distilled from lithium aluminium hydride under dry nitrogen:[9] b.p., 65° at 742 mm, v.p. 147 mm at 29°, 70 mm at 0°. Ethyl ether (Mallinckrodt) was treated with calcium hydride for 24 hr, and distilled from the hydride directly into the line: v.p. 189 mm at 0°. Dimethyl ether (Matheson) was purified by distillation in the vacuum apparatus: v.p. 35 mm at −78°.

Acetone was dried over anhydrous calcium sulphate, distilled through a 50 plate column: b.p., 56° at 748 mm, n_D^{20} 1·3590. Ethylene was obtained from a commercial cylinder and used directly.

Reaction of diborane with boron trichloride in diglyme. Into the reaction vessel was placed 2·5 ml of diglyme and 0·500 mmole of diborane. The pressure in the flask at 25° was 71 mm. Boron

* Research with Dr. B. C. SUBBA RAO.

[7] H. C. BROWN and R. R. HOLMES, *J. Amer. Chem. Soc.* **78**, 2173 (1956).
[8] R. T. SANDERSON, *Vacuum Manipulations of Volatile Compounds.* Wiley, New York (1947).
[9] T. HIGUCHI, *Analyt. Chem.* **22**, 534 (1950); *J. Amer. Chem. Soc.* **73**, 2676 (1951).

trichloride was condensed into the flask. The pressure dropped rapidly. After 24 hr, the pressure was 4 mm at room temperature.

Preparation of monochloroborane etherate from sodium borohydride and boron trichloride in diglyme. In a 50 ml round-bottom flask was placed 4·00 ml of a 1·01 M solution of sodium borohydride in diglyme, followed by 4·00 ml of a 1·00 M solution of boron trichloride in tetrahydropyran. A white precipitate formed, along with traces of a gas. The precipitate was allowed to settle for 1 hr, then a 2·00 ml sample of the clear solution was removed and analysed for boron, chloride and active hydrogen. The results, 1·93 mmoles of boron, 1·96 mmoles of chloride and 3·90 mmoles of hydrogen, correspond to the formation of the monochloroborane derivative.

Preparation of monochloroborane–tetrahydropyran. In a reaction flask of 15 ml capacity were introduced 0·552 mmole of tetrahydropyran, 0·184 mmole of diborane and 0·184 mmole of boron trichloride. The liquid nitrogen bath was removed and the materials permitted to warm up. Near room temperature a vigorous reaction occurred with the formation of a white solid, and the pressure decreased to almost zero. The product melted at 19–20°.

Preparation of monochloroborane–tetrahydrofuran. The procedure and quantities were identical with the above experiment. The product consisted of large, triangular shaped crystals, m.p. −38 to −36°.

Preparation of monochloroborane–ethyl ether. In the flask were condensed 1·00 mmole of diborane, 1·00 mmole of boron trichloride and 3·00 mmoles of ethyl ether. After 40 hr, the pressure was 14 mm. Traces of volatile impurities were removed, with the flask cooled to −78°. The residue melted over a wide range, −85 to −105°.

Preparation of monochloroborane–methyl ether. In a 4 ml tube fitted with a break-tip were condensed 2·00 mmoles of dimethyl ether, 0·67 mmole of boron trichloride and 1·34 mmoles of diborane. The sealed tube was allowed to stand at room temperature for 36 hr. The tube was opened and gases volatile at −80° removed. There was collected 0·67 mmole of diborane. Thus, the reactants had interacted in the ratio, 1·00 B_2H_6 : 1·00 BCl_3 : 3·00 $(CH_3)_2O$, to form the product, m.p. −20 to −21°.

Preparation of dichloroborane–tetrahydropyran. Boron trichloride, 0·270 mmole, diborane, 0·093 mmole were placed in the reaction tube with 0·555 mmole of tetrahydropyran. The materials reacted to produce a white solid, m.p. 10–15°.

Preparation of dichloroborane–ethyl ether. Into the reaction vessel were condensed 0·67 mmole of boron trichloride, 1·72 mmoles of ethyl ether and 0·17 mmole of diborane. The reaction was permitted to proceed at room temperature for 1 hr, following which the excess ether was removed at low temperature. There was obtained 0·71 mmole. The material in the flask was a white solid, m.p. −25 to −30°.

Reaction of monochloroborane–tetrahydropyran with acetone and ethyl acetate. The following experiments are typical of those carried out to explore the reducing action of these reagents towards typical organic derivatives. A sample of monochloroborane–tetrahydropyran, 0·555 mmole, was prepared from the components. On treatment with water in the reaction vessel the pressure of hydrogen developed was 280 mm. An identical sample, 0·555 mmole, was treated with approximately 1 ml of acetone (excess). After 30 min, the reaction mixture was hydrolysed. No hydrogen was formed.

In a similar experiment, 0·555 mmole of the complex was treated with 1 ml of ethyl acetate (excess). After 1 hr, the reaction mixture was hydrolysed. The hydrogen evolved developed a pressure of 277 mm.

Reaction of dichloroborane–tetrahydropyran with ethylene. Into an ampoule fitted with two break-tips were condensed 0·185 mmole of diborane, 0·740 mmole of boron trichloride and 1·11 mmole of tetrahydropyran. The tube was sealed. After 24 hr at room temperature, it was opened to the line. The pressure was less than 1 mm. Ethylene, 5·57 mmoles, was introduced and the reaction sealed and allowed to stand at room temperature for 2 weeks.* The tube was opened and the products distilled. There was obtained 4·44 mmoles of ethylene. The material volatile at 40° was exposed to oxygen. It ignited instantly, indicating the formation of boron–carbon bonds. The residue in the tube which was not volatile was hydrolysed and analysed for boron and chloride. There were found 0·67 mmole boron and 2·07 mmoles chloride.

* The long reaction time is not essential. In later work we have observed rapid reactions with a number of olefins. Work in progress with Dr. B. C. Subba Rao. With shorter reaction times the alkyl chloroboranes can be isolated. The disproportionation which was here observed was apparently a consequence of the long reaction time.

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THE PREPARATION AND CRYSTAL STRUCTURE OF GALLIUM TRIFLUORIDE

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Abstract—The preparation of pure gallium trifluoride by heating gallium in hydrogen fluoride at 550° is described. Modifications to existing analytical methods, which permit gallium and fluoride to be determined in the presence of one another, are also reported.

The crystal structure of gallium trifluoride has been elucidated. The unit cell is a bimolecular rhombohedron of dimensions $a = 5{\cdot}20 \pm 0{\cdot}01$ Å. $\alpha = 57{\cdot}5°$. There are two Ga atoms in the special positions 000; $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ of $R\bar{3}c$ and six *F* atoms at $x, \frac{1}{4} - x, \frac{1}{4}$; $\frac{1}{4} - x, \frac{1}{4}, x$; $\frac{1}{4}, x, \frac{1}{4} - x$; $\bar{x}, \frac{1}{4} + x, \frac{3}{4}$; $\frac{1}{4} + x, \frac{3}{4}, \bar{x}$; $\frac{3}{4}, \bar{x}, \frac{1}{4} + x$, where $x = -0{\cdot}136$. GaF_3 is isostructural with FeF_3.

Preliminary work on ammonium tetrafluogallate indicates that it is isomorphous with ammonium tetrafluoaluminate, having a tetragonal unit cell of dimensions $a = 3{\cdot}71$ Å, $c = 6{\cdot}39$ Å.

PRIOR to attempts by us to obtain lower fluorides of gallium, it was necessary to prepare pure gallium trifluoride. None of the methods mentioned in the literature was found suitable but the reaction between anhydrous hydrogen fluoride and gallium metal at elevated temperatures yielded a pure, crystalline specimen of gallium trifluoride.

The crystal structures of the Group IIIB trifluorides have not been fully established. From considerations of molar volumes, HANNEBOHN and KLEMM[1] concluded that GaF_3 and InF_3 probably have structures similar to that of AlF_3 but different from that of TlF_3. Other metallic trifluorides, such as FeF_3 and ScF_3, have structures related to that of AlF_3. The unit cells are rhombohedral, with the fluoride ions approximately close-packed and the metal ions situated in certain octahedral holes between them. Recently, the work of JACK *et al.*[2] has shown that the structures of many metallic trifluorides fall into three types: (a) those in which the fluoride ions are in cubic close packing, typified by MoF_3 and TaF_3; (b) those in which the fluoride ions are in hexagonal close packing, as, for example, RhF_3, PdF_3 and IrF_3; (c) those in which the arrangement of fluoride ions is intermediate between the first two types, such as the trifluorides of the first transition series and RuF_3. The ionic radius of Ga^{3+} (0·62 Å) is very similar to the radii of the trivalent ions of the first transition series. If the structure adopted by the trifluoride depends largely on ionic size, then GaF_3 might be expected to have a structure very similar to the structures of FeF_3 and CoF_3, where the cationic radii are 0·67 Å and 0·65 Å respectively. An X-ray investigation of its crystal structure has confirmed that GaF_3 is isostructural with the trifluorides of the first transition series.

EXPERIMENTAL

Preparation of gallium trifluoride

The only recorded preparation of GaF_3 is that of HANNEBOHN and KLEMM[1] who obtained it as a white powder by the thermal decomposition of ammonium hexafluogallate in a stream of dry fluorine. We were unable to prepare pure GaF_3 by this method.

[1] O. HANNEBOHN and W. KLEMM, *Z. Anorg. Chem.* **229**, 337 (1936).
[2] H. J. JACK, R. D. PEACOCK and G. J. WESTLAND, *Acta Cryst.* **10**, 63 (1957).

The thermal decomposition of ammonium hexafluogallate may follow two courses depending on whether hydrogen fluoride or ammonium fluoride is eliminated. Thus:

$$(NH_4)_3GaF_6 \xrightarrow{-NH_4F} (NH_4)_2GaF_5 \xrightarrow{-NH_4F} (NH_4)GaF_4 \xrightarrow{-NH_4F} GaF_3$$

$$(NH_4)_2GaF_5 \xrightarrow{-HF} Ga(NH_2)F_2 \xrightarrow{-HF} Ga(NH)F \xrightarrow{-HF} GaN$$

the second sequence being postulated by HANNEBOHN and KLEMM to explain the weight changes observed on heating ammonium hexafluogallate *in vacuo*.

In the present work, ammonium hexafluogallate (prepared by the method of PUGH[3]) was heated in a stream of dry fluorine at 400°C for several hours until the residue did not change in weight on further heating. The residue did not analyse for the composition GaF_3. (Found: Ga, 51·72, F, 44·06; Calc. for GaF_3: Ga, 55·00, F, 45·00%.) A powder diagram showed lines which were not due to GaF_3. The purity of the product was not improved by sublimation at 900–1000°C in a silica apparatus.

EINECKE[4] has stated that anhydrous GaF_3 may be prepared by heating ammonium hexafluogallate in nitrogen but gave no details. According to our observations, the principal product of this reaction at temperatures above 700° is gallium nitride and this seems likely in view of the fact that HAHN and JUZA[5] prepared gallium nitride by heating ammonium hexafluogallate in ammonia at 900°.

Heating ammonium hexafluogallate *in vacuo* or in nitrogen at 220° yielded ammonium tetrafluogallate, NH_4GaF_4, which confirms EINECKE's statement that this compound is formed by the mild thermal decomposition of the hexafluogallate. Some X-ray data on this substance are given later. Heating the hexafluogallate at higher temperatures *in vacuo* apparently yielded a mixture of GaN and Ga(NH)F.

As none of the methods mentioned in the literature gave pure GaF_3, other methods were tried. Direct union of the elements was found to be unsatisfactory, for at the temperatures which could be used in the nickel apparatus available, the surface film of GaF_3 which formed on the molten gallium was practically involatile.

The best method was found to be the reaction between gallium metal and anhydrous hydrogen fluoride. No report of this reaction was found in the literature.

Hydrogen fluoride was passed through a nickel tube over metallic gallium contained in a nickel boat at 550° with nitrogen as a carrier gas. After several hours the gallium was covered with a thick crust of a white, crystalline substance and the inner walls of the boat were covered with colourless needles. An X-ray powder diagram showed lines due to GaF_3 only and analysis confirmed the composition: (Found: Ga, 54·86, F, 44·81; Calc.: Ga, 55·00, F, 45·00%). It is likely that this method would be much improved if higher temperatures could be used to sublime off GaF_3 as it forms, but we were limited to 550° by silver-soldered joints on our apparatus.

Gallium trifluoride, as thus prepared, is a white, crystalline solid, insoluble in water and dilute acids but soluble in caustic alkalis. It is apparently quite stable in air, for no change was observed over a period of several weeks.

Analysis

(*a*) *Fluoride*. The determination of fluoride ion in the presence of gallium is complicated by the ready formation of the GaF_6^{3-} complex ion in aqueous solution. The common gravimetric method of estimating fluoride as lead chlorofluoride does not give good results in the presence of gallium, according to HANNEBOHN and KLEMM. Attempts were made to separate the fluoride from gallium by the WILLARD and WINTER method[6] but we could not achieve complete distillation of the fluoride as fluosilicic acid. Aluminium is known to interfere with this reaction and gallium apparently behaves likewise.

Various volumetric methods were also tried but none was found in the literature which could be used in the presence of gallium. Separation of the gallium as oxinate into a chloroform phase was tried but still without success.

[3] W. PUGH, *J. Chem. Soc.* 1046, 1959 (1937).
[4] E. EINECKE, *Das Gallium*. Leopold Voss, Leipzig (1937).
[5] H. HAHN and R. JUZA, *Z. Anorg. Chem.* **244**, 111 (1940).
[6] H. H. WILLARD and O. B. WINTER, *Industr. Engng. Chem.* (*Anal.*) **5**, 7 (1933).

The method finally adopted was a modification of the method of ROWLEY and CHURCHILL,[7] whereby the fluoride ion concentration is determined by titration with thorium nitrate solution in the presence of a monochloracetate buffer and Alizarin Red S as indicator. Gallium interferes with this titration by forming a lake with the Alizarin Red S. However, if the Ga^{3+} ion is removed by complexing with the exact equivalent of ethylenediaminetetracetic acid the thorium nitrate titration may be carried out normally.

(*b*) *Gallium.* DOLEŽAL *et al.*[8] have shown that gallium may be successfully determined in the presence of fluoride ions. In this method, morin is used as an indicator since the gallium–morin complex fluoresces strongly under ultra-violet light. EDTA destroys the complex and the end-point is clearly indicated by the quenching of the fluorescence. We have found that this method in combination with the modified ROWLEY and CHURCHILL method enables both gallium and fluorine to be determined quickly and accurately when they are present in the same solution.

The procedure finally adopted to estimate both gallium and fluorine was as follows. The gallium content of an unknown solution was determined by the EDTA–morin method of DOLEŽAL *et al.* A fresh aliquot of the same solution was then treated with the exact equivalent of EDTA solution to complex all the gallium and titrated with thorium nitrate following the directions of ROWLEY and CHURCHILL. The maximum error in gallium estimation in aliquots containing about 20 mg Ga was −0·25 per cent. The error in fluoride estimation on similar amounts was ±0·3 per cent.

DETERMINATION OF THE STRUCTURE OF GaF_3

The crystals of gallium trifluoride which grew around the edges of the nickel boat were in the form of long needles, up to 1 cm in length but only a few hundredths of a mm in thickness. These needles were shown by the polarizing microscope to be single crystals. They were a suitable shape for oscillation about the needle axis, which was found to coincide with a crystal axis, but awkward to mount for rotation about other axes. Some plate-like crystals were also observed but these all proved to be multiple twins and unsuitable for X-ray work. Due to the unsuitable shape of the crystals, intensity measurements other than from photographs with oscillation about the needle axis, were not of the highest accuracy. Relative intensities were estimated by visual comparison and by a microdensitometer, with good agreement between the two sets of results. The structure was elucidated from two projections.

Oscillation and zero-layer Weissenberg photographs were taken about the needle axis and an axis perpendicular to this, using CuKα radiation. Weissenberg photographs taken with oscillation about the needle axis showed hexagonal symmetry. The reflections were indexed on the basis of a hexagonal cell with $a = b = 5{\cdot}00$ Å. The length of the c (needle) axis was measured from oscillation photographs and a zero-layer Weissenberg photograph about b; $c = 12{\cdot}97$ Å. Reflections $hkil$ were present only when $h - k + l = 3n$. In addition, reflections of the type $h0\bar{h}l$ were present only when $l = 2n$. The possible space groups were therefore limited to $R3c$ or $R\bar{3}c$. Tests for pyroelectric and piezoelectric effects were negative and the centro-symmetric space group $R\bar{3}c$ was therefore adopted with the usual reservations.

There are 6 GaF_3 molecules per hexagonal unit cell. The general position in $R\bar{3}c$ is 36-fold, hence the Ga^{3+} and F^- ions must occupy special positions. The possible sets of 6-fold special positions both place the Ga^{3+} ions along the c axis. It was argued that a Patterson synthesis projected perpendicular to c would give directly the positions of the F^- ions relative to Ga^{3+} ions at the origin of the [001] projection. The two-dimensional Patterson function was summed for all values of $F^2(hk.0)$ and revealed large peaks at $x = \frac{1}{3}$, $y = 0$ and at positions related to this by a hexad axis through the

[7] R. J. ROWLEY and H. V. CHURCHILL, *Industr. Engng. Chem.* (*Anal.*) **9**, 551 (1937).

[8] J. DOLEŽAL, V. PATROVSKÝ, Z. ŠULCEK and J. ŠVASTA, *Chem. Listy* **40**, 1517 (1955).

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origin. The only 18-fold position of $R\bar{3}c$ consistent with the Patterson projection is position (d) of the *International Tables for Crystal Structure Determination*, namely $x\ 0\ \frac{1}{4}$ and equivalent positions. The value of x appeared to be close to $\frac{1}{3}$.

The special positions occupied by the gallium atoms ensure that all gallium contributions to the structure amplitudes are in phase for all permitted reflections. For all angles of reflection the atomic scattering factor of gallium is approximately equal to three times the scattering factor of fluorine. Except for vanishingly small amplitudes, the structure factors are thus all of the same sign. Taking all the signs to be positive, a Fourier synthesis of electron density was summed over all values of $F_{obs}(hk.0)$. The number of independent terms was very small due to the small size of the unit cell and the many rhombohedral absences. Termination of series errors were therefore serious, and, although the positions of the fluorine atoms were clearly indicated, some large spurious peaks were present. Fourier refinement was in any case impossible as the signs of all the reflections were already determined. The fluorine atoms were clearly close to $x = \frac{1}{3}$, $y = 0$ etc. but the shape of the large peak in this position indicated that x should be somewhat larger than $\frac{1}{3}$.

An electron density projection perpendicular to [010] using values of $F_{obs}(h0.l)$ phased on gallium atoms at 000 and $00\frac{1}{2}$ (position (a) of the *International Tables*) showed gallium peaks in the assumed positions and fluorine peaks in the positions $x \simeq 0{\cdot}38$, $z = \frac{1}{4}$ etc. Again there were spurious peaks due to termination of series errors.

Projections of electron density perpendicular to [010] and [001] were made by using as coefficients the final values of $F_{calc}(h0.l)$ and $F_{calc}(hk.0)$ respectively, calculated from the final fluorine parameter. In each case, the electron density map matched in all respects the corresponding F_{obs} syntheses, including the peaks due to termination of the series.

A difference synthesis of $[F_{obs}(h0.l) - F_{calc}(h0.l)]$ was carried out but only a very slight shift of the F atoms was indicated. Refinement of the structure was therefore carried out graphically by plotting values of F_{calc} $(hk.0)$ and F_{calc} $(h0.l)$ for a series of x values from 0·370 to 0·400. The best agreement was obtained when $x = 0{\cdot}386$. Table 1 lists the values of F_{obs} and F_{calc} for the two zones $hk.0$ and $h0{\cdot}l$.

A Wilson plot to determine the temperature factor showed this to be negligible. The disagreement factor $R = \Sigma\left|F_{obs} - F_{calc}\right| / \Sigma\left|F_{obs}\right|$ was 0·11 for the $hk.0$ zone and 0·165 for the $h0.l$ zone. The absorption errors in the measured intensities of the $h0.l$ zone of reflections are likely to be significant, due to the shape of the crystal. It was not considered worthwhile to correct for absorption or to attempt a three-dimensional refinement since no great interest attaches to very precise location of the fluorine atoms in the unit cell. The error in F atom positions is estimated as $\pm 0{\cdot}01$ Å.

Description of the structure

The unit cell of gallium trifluoride is a bimolecular rhombohedron with space group symmetry $R\bar{3}c$. The unit cell dimensions are: $a_R = 5{\cdot}20 \pm 0{\cdot}01$ Å; $\alpha_R = 57{\cdot}5°$. The atoms lie in the following special positions of $R\bar{3}c$:

2 Ga at 0 0 0; $\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}$. (Position (b) of the *International Tables*).

6 F at $x, \frac{1}{2} - x, \frac{1}{4}$; $\frac{1}{2} - x, \frac{1}{4}, x$; $\frac{1}{4}, x, \frac{1}{2} - x$.

$\bar{x}, \frac{1}{2} + x, \frac{3}{4}$; $\frac{1}{2} + x, \frac{3}{4}, \bar{x}$; $\frac{3}{4}, \bar{x}, \frac{1}{2} + x$.

(Position (e) of the *International Tables*) where $x = -0{\cdot}136$.

The structure of the rhombohedral cell is shown in Fig. 1. Referred to hexagonal axes, the hexagonal pseudo-cell has the dimensions: $a = b = 5{\cdot}00 \pm 0{\cdot}01$ Å; $c = 12{\cdot}97 \pm 0{\cdot}02$ Å. This hexamolecular cell contains 18 F at (0 0 0; $\frac{1}{3}\,\frac{2}{3}\,\frac{1}{3}$; $\frac{2}{3}\,\frac{1}{3}\,\frac{2}{3}$;)

TABLE 1.—COMPARISON OF OBSERVED AND CALCULATED STRUCTURE FACTORS FOR GaF_3

$h\,k\,l$	F_{calc}	F_{obs}	$h\,k\,l$	F_{calc}	F_{obs}
1 1 0	88	88	0 0 12	150	114
2 2 0	92	91	3 0 12	109	104
3 3 0	86	106	1 0 14	90	96
			2 0 $\bar{2}$	91	82
4 1 0	73	84	5 0 $\bar{2}$	38	57
3 0 0	168	188	1 0 $\bar{4}$	124	98
1 0 2	176	133	4 0 $\bar{4}$	77	102
4 0 2	110	119	0 0 $\bar{6}$	30	45
2 0 4	170	169	3 0 $\bar{6}$	61	80
5 0 4	112	112	2 0 $\bar{8}$	138	102
0 0 6	30	45	1 0 $\bar{10}$	116	114
3 0 6	61	80	3 0 $\bar{12}$	109	104
1 0 8	107	104	2 0 $\bar{14}$	60	45
4 0 8	64	96	1 0 $\bar{16}$	65	47
2 0 10	74	86	4 0 $\bar{10}$	88	98

$+(x\,0\,\frac{1}{4};\ 0\,x\,\frac{1}{4};\ \bar{x}\,\bar{x}\,\frac{1}{4};\ \bar{x}\,0\,\frac{3}{4};\ 0\,\bar{x}\,\frac{3}{4};\ x\,x\,\frac{3}{4})$ where $x = 0{\cdot}386$ and 6 Ga at (0 0 0; $\frac{1}{3}\,\frac{2}{3}\,\frac{1}{3}$; $\frac{2}{3}\,\frac{1}{3}\,\frac{2}{3}$;) + (0 0 0; $0\,0\,\frac{1}{2}$).

The structure consists of layers of more or less close packed fluoride ions with gallic ions occupying certain octahedral holes between them. Each gallium atom has

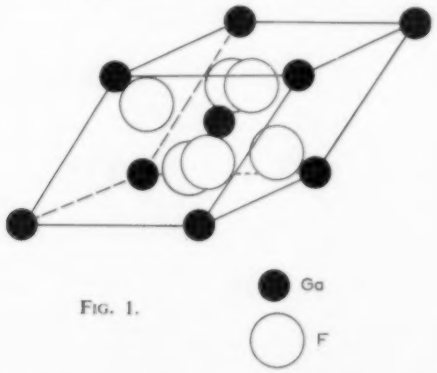

FIG. 1.

six fluorine neighbours at a distance of 1·89 Å. (Sum of ionic radii = 1·95 Å.) Each fluorine atom has four neighbours in its own layer at 2·69 Å and four others in adjacent planes at 2·67 Å. Each fluorine atom lies equidistant from two gallium atoms but slightly displaced from the line joining them. The Ga–F–Ga angle is 145°. The closest approach of gallium atoms to one another is 3·61 Å.

The structure very closely resembles that of cobaltic fluoride found by JACK[2] and is similar to the structures of all the trifluorides of the first transition series. Table 2, below,

TABLE 2

	Cation radius (Å)	Unit cell dimensions			
		Rhombohedral		Hexagonal	
		a_R (Å)	α_R	a_H (Å)	c_H (Å)
FeF_3	0·67	5·362	57·99	5·198	13·331
CoF_3	0·65	5·279	56·97	5·035	13·218
GaF_3	0·62	5·20	57·5	5·00	12·97
	M–F (Å)	F–F		M–F–M angle (degrees)	F parameter x
		(i) (Å)	(ii) (Å)		
FeF_3	1·92	2·72	2·72	153	−0·164
CoF_3	1·89	2·66	2·69	149	−0·15
GaF_3	1·89	2·69	2·67	145	−0·136

TABLE 3

d (observed)	Plane_{hex}	d (calculated)	Intensity	Plane_{Rh}
4·115	1 $\bar{1}$ 1	4·110	*vw*	1 0 0
3·610	1 0 2	3·603	*vs*	1 1 0
2·600	1 0 $\bar{4}$	2·599	*s*	$\bar{1}$ $\bar{1}$ $\bar{2}$
	1 $\bar{1}$ 4	2·600		2 1 1
2·491	1 1 0	2·500	*m*	0 1 $\bar{1}$
2·162	0 0 6	2·167	*s*	2 2 2
	0 0 $\bar{6}$	2·167		$\bar{2}$ $\bar{2}$ $\bar{2}$
	1 1 3	2·165		1 2 0
2·044	2 0 $\bar{2}$	2·055	*w*	0 0 $\bar{2}$
1·799	2 0 4	1·802	*s*	2 2 0
1·636	1 1 6	1·637	*s*	2 3 1
1·622	2 1 $\bar{1}$	1·624	*vw*	0 1 $\bar{2}$
1·580	2 1 2	1·587	*s*	1 2 $\bar{1}$
1·514	1 0 8	1·521	*m*	3 3 2
1·456	2 1 $\bar{4}$	1·462	*m*	$\bar{1}$ 0 $\bar{3}$
1·437	3 0 0	1·443	*m*	1 1 $\bar{2}$
1·382	2 1 5	1·385	*vw*	2 3 0
1·301	2 0 $\bar{8}$	1·300	*m*	$\bar{2}$ $\bar{2}$ $\bar{4}$
1·248	1 0 $\bar{1}\bar{0}$	1·245	*wm*	$\bar{3}$ $\bar{3}$ $\bar{4}$
	2 2 0	1·250		0 2 $\bar{2}$
	1 1 9	1.251		3 4 2

TABLE 3 (*continued*)

d (observed)	Plane$_{hex}$	*d* (calculated)	Intensity	Plane$_{Rh}$
1·201	2 2 3	1·201	*w*	1 3 $\bar{1}$
	3 0 6	1·201		3 3 0
	3 0 $\bar{6}$	1·201		$\bar{1}$ $\bar{1}$ $\bar{4}$
1·193	3 1 1	1·196	*vw*	1 2 $\bar{2}$
1·177	3 1 $\bar{2}$	1·181	*wm*	0 1 $\bar{3}$
1·153	2 1 8	1·153	*wm*	3 4 1
1·124	3 1 4	1·126	*w*	2 3 $\bar{1}$
1·118	2 0 10	1·115	*vw*	4 4 2
1·088	3 1 $\bar{5}$	1·091	*w*	$\bar{1}$ 0 $\bar{4}$
1·080	0 0 12	1·083	*vw–w*	4 4 4
	2 2 6	1·083		2 4 0
1·064	4 0 2	1·067	*vw–w*	2 2 $\bar{2}$
1·025	4 0 $\bar{4}$	1·028	*vw*	0 0 $\bar{4}$
1·018	2 1 $\bar{10}$	1·018	*w*	$\bar{3}$ $\bar{2}$ $\bar{3}$
1·009	3 1 7	1·008	*vw*	3 4 0
0·996	3 2 $\bar{1}$	0·992	*w*	0 2 $\bar{3}$
	1 1 12	0·995		4 5 3
0·979	3 2 2	0·983	*w*	1 3 $\bar{2}$
	1 $\bar{1}$ 13	0·974		5 4 4
0·965	2 1 11	0·959	*w*	4 5 2
	3 1 $\bar{8}$	0·966		2 1 5
0·947	3 2 $\bar{4}$	0·950	*wm*	$\bar{1}$ 1 $\bar{4}$
0·942	2 2 9	0·945	*w*	3 5 1
	4 1 0	0·945		1 2 $\bar{3}$
0·911	1 0 14	0·908	*w*	5 5 4
0·899	4 0 8	0·901	*vw–w*	4 4 0
0·882	3 1 10	0·883	*w*	4 5 1
0·867	3 0 12	0·867	*wm*	5 5 2
	3 0 $\bar{12}$	0·867		$\bar{3}$ $\bar{3}$ $\bar{6}$
	4 1 6	0·867		3 4 $\bar{1}$
0·862	5 0 $\bar{2}$	0·858	*w*	1 1 $\bar{4}$
0·856	2 0 $\bar{14}$	0·854	*w*	$\bar{4}$ $\bar{4}$ $\bar{6}$
	2 1 $\bar{13}$	0·854		$\bar{4}$ $\bar{3}$ $\bar{6}$
	3 2 7	0·857		$\bar{2}$ 0 $\bar{5}$
0·847	3 1 $\bar{11}$	0·842	*w*	$\bar{3}$ $\bar{2}$ $\bar{6}$
	3 2 8	0·847		3 5 0
0·835	5 0 4	0·837	*w*	3 3 $\bar{2}$
0·831	4 0 $\bar{10}$	0·832	*w*	$\bar{2}$ $\bar{2}$ $\bar{6}$
	3 3 0	0·833		0 3 $\bar{3}$
0·819	3 3 3	0·818	*w*	1 4 $\bar{2}$
	1 1 15	0·819		5 6 4
	2 2 12	0·819		4 6 2
0·814	4 2 1	0·816	*vw*	1 3 $\bar{3}$
0·810	3 1 1	0·808	*wm*	1 2 $\bar{2}$
0·801	1 0 $\bar{16}$	0·799	*vw*	$\bar{5}$ $\bar{5}$ $\bar{6}$
0·791	4 1 9	0·791	*w*	4 5 0
	4 2 4	0·793		2 4 $\bar{2}$
0·789	3 2 $\bar{10}$	0·789	*vw–w*	$\bar{3}$ $\bar{1}$ $\bar{6}$
0·776	3 3 6	0·777	*w*	2 5 $\bar{1}$

shows the similarity between the structures of FeF_3 and CoF_3, as determined by JACK, and the structure of GaF_3.

Table 3 lists the interplanar spacings and observed intensities of a powder diagram of pure gallium trifluoride using filtered CuKα radiation. All powder photographs were taken with an 11·5 cm diameter camera with Ievens–Straumanis asymmetric film mounting.

TABLE 4

d (observed)	Plane	*d* (calculated)	Intensity
6·39	0 0 1	6·39	*s*
3·71	1 0 0	3·71	*s*
3·20	1 0 1	3·208	*s*
	0 0 2	3·200	
2·623	1 1 0	2·624	*m*
2·429	1 0 2	2·421	*vw*
	1 1 1	2.426	
2·127	0 0 3	2·130	*m*
1·851	1 0 3	1·847	*s*
	2 0 0	1·855	
1·788	2 0 1	1·782	*mw*
1·659	2 1 0	1·659	*m*
	1 1 3	1·654	
1·607	2 0 2	1·604	*m*
	0 0 4	1·600	
	2 1 1	1·606	
1·473	1 0 4	1·467	*w*
	2 1 2	1·473	
1·406	2 0 3	1·399	*w*
1·370	1 1 4	1·364	*w*
1·316	2 2 0	1·312	*m*
	2 1 3	1·309	
1·288	0 0 5	1·278	*w*
	2 2 1	1·285	
1·217	1 0 5	1·208	*w*
	2 0 4	1·211	
	2 2 2	1·213	
	3 0 1	1·214	
1·179	3 1 0	1·173	*w*
1·158	1 1 5	1·148	*w*
	2 1 4	1·151	
	3 0 2	1·154	

Unit cell dimensions and space group of ammonium tetrafluogallate

A pure specimen of ammonium tetrafluogallate was obtained by heating ammonium hexafluogallate in a stream of nitrogen at 220°C, until no further change in weight occurred. 0·1154 g $(NH_4)_3GaF_6$ gave 0·0793 g of residue. (Calc. for NH_4GaF_4 0·0795 g). The product was a pure white powder. (Found: Ga, 42·6; F, 45·9; Calc. for NH_4GaF_4: Ga, 42·6; F, 46·4%.)

Table 4 lists the values of *d*(*hkl*) and relative intensities of the reflections obtained from a powder diagram of NH_4GaF_4 taken with CuKα radiation. All the observed

lines could be indexed on the basis of a tetragonal unit cell of dimensions $a = 3{\cdot}71$ Å, $c = 6{\cdot}39$ Å. There are no systematic absences; the space group is therefore limited to $P4/mmm$.

The crystal structures of several tetrafluoaluminates have been reported. The unit cells are all tetragonal and the space groups are all $P4/mmm$. For comparison the unit cell dimensions of some tetrafluoaluminates are given below.

Aluminate	a (Å)	c (Å)
$KAlF_4$	3·55	6·14
NH_4AlF_4	3·59	6·35
$RbAlF_4$	3·62	6·26
$TlAlF_4$	3·61	6·37

It appears that NH_4GaF_4 is isomorphous with these tetrafluoaluminates. A complete structure analysis has not been attempted.

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SPINEL PHASE IN THE SYSTEM $MgO—Fe_2O_3—Al_2O_3$

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Abstract—The three component system $MgO—Fe_2O_3—Al_2O_3$ has been investigated at 1250°C and at 1400°C. The binary parts of this system, already described some twenty years ago, are reviewed and completed. The ternary diagram shows a broad spinel area: this area increases with increasing temperatures. Our preparations do not contain Fe^{2+} ions, as was ascertained by analytical methods and by d.c. resistivity measurements. The resistivity has a fairly high value. The physical properties are roughly in agreement with the properties already found in systems investigated previously. Substituting Al^{3+} ions for Fe^{3+} ions in the spinel phase lowers the value of the magnetic saturation and the Curie temperature. An increasing amount of Fe_2O_3 in the spinel phase increases the magnetic saturation and the Curie temperature. Samples with the composition of a mineral called "hoegbomite" have been investigated and the possible structure of this mineral is discussed.

IN an attempt to prepare a compound with a composition $Mg(Fe, Al)_4O_7$ we found results which were remarkable enough for a more extensive investigation of the system $MgO—Al_2O_3—Fe_2O_3$. In this ternary system the two component systems $MgO—Fe_2O_3$ and $MgO—Al_2O_3$ have already been the subject of investigation in the early years of ferrite research. In 1936 VAN ARKEL, VERWEY and VAN BRUGGEN[1] observed that ferrites are able to dissolve considerable quantities of Fe_2O_3, especially at higher temperatures.

The term "dissolve" means that the specific lines of Fe_2O_3 (hematite) on the X-ray diffraction diagram have disappeared and that this diagram shows only one phase. The authors explain this solubility by a configuration of Fe_2O_3: γ-Fe_2O_3, which has a structure closely related to the spinel structure as was found in 1935 by several authors.[2] Another point made clear was that compounds with a composition $MeO : Fe_2O_3 = 2 : 3$ (Me = Zn, Mg, Ni, etc), as mentioned by HILPERT,[3] do not exist.

In the two-component system $MgO—Al_2O_3$ one can expect the same behaviour, as $MgAl_2O_4$ is also able to dissolve Al_2O_3 and as Al_2O_3 can assume the spinel structure as the metastable γ-Al_2O_3. This γ-Al_2O_3 can be stabilized by solid-solution formation with another compound having spinel structure: $MgAl_2O_4$.[4]

Only a few minerals with excess Fe_2O_3 are known e.g. a spinel from the Vesuvius[5] with composition $MgO : FeO_{1.5} = 1 : 3{\cdot}49$. The natural spinel $MgAl_2O_4$ with excess Al_2O_3 is a subject of discussion in recent Russian literature.[6]

[1] A. E. VAN ARKEL, E. J. W. VERWEY and M. J. VAN BRUGGEN, *Rec. Trav. Chim.* **55**, 331 (1935).
[2] E. J. W. VERWEY, *Z. Krist.* **91**, 65 (1935); G. HÄGG, *Z. Phys. Chem.* B **29**, 95 (1935); E. KORDES, *Z. Krist.* **91**, 193 (1935); G. W. v. OOSTERHOUT and C. J. W. ROOYMANS, *Nature, Lond.* **181**, 44 (1958).
[3] S. HILPERT, A. WILLE and A. LINDNER, *Z. Phys. Chem.* B **18**, 291 (1932); **22**, 395 (1933).
[4] F. RINNE, *Neues Jahrb. Min. Geol.* A **58**, 43 (1928); G. HÄGG and G. SÖDERHOLM, *Z. Phys. Chem.* B **29**, 88 (1935); D. M. ROY, R. ROY and E. F. OSBORN, *Amer. J. Sci.* **251**, 337 (1953); H. SAALFELD and H. JAGODZINSKI, *Z. Krist.* **109**, 87 (1957).
[5] H. BERMAN and C. FRONDEL, *Dana's System of Minerology* (Edited by C. PALACHE) p. 701. Wiley, New York (1946).
[6] V. V. LAPIN, *C. R. Acad. Sci. U.R.S.S.* **104**, 611 (1955).

At the other side of the two-component system we have a two-phase line of MgO and $MgFe_2O_4$, and MgO and $MgAl_2O_4$. The two compounds MgO and $MgFe_2O_4$ do not dissolve in each other.

Much work has been done in the system Fe_2O_3—Al_2O_3; these two oxides have the same rhombohedral structure but they do not form a complete series of solid solutions. Since the unit-cell dimensions differ by more than 5 per cent one cannot expect a continuous series of mixed crystals. The data given in the literature about the limits of solubility of the oxides do not agree. In a recent investigation MUAN and GEE[7] reviewed the solubility data and described a new compound $FeAlO_3$, formed above 1318°C.

Another well-known two-component system in this ternary diagram is that of $MgFe_2O_4$—$MgAl_2O_4$. Results given in the literature do not agree and we will compare our results with those given by different authors.[8,9]

In this present report an investigation on the three component system

$$MgO—Fe_2O_3—Al_2O_3$$

is described; special attention has been given to the spinel phase.

Two firing temperatures were chosen:

1. 1250°C, firing the samples in air
2. 1400°C, firing the samples in oxygen

At the higher temperature of 1400°C, it is advisable to fire in oxygen, since at this temperature ferric oxide begins to dissociate. In order to be certain that there was no such reduction in our 1250°C and 1400°C series, an analysis* of the Fe^{2+} content was carried out for most of the samples. It appeared that the Fe^{2+} content was in no case more than 0·2 per cent. Another more qualitative measure for Fe^{2+} content in samples with a Fe : Al ratio greater than one is the value of the resistivity. In all our samples the resistivity was high: about 10^7 ohm cm. We conclude that in our materials Fe^{2+} ions were practically absent.

EXPERIMENTAL METHOD

A large number of samples with different compositions in the system $MgO—Al_2O_3—Fe_2O_3$ were prepared from the starting materials MgO, Al_2O_3 and Fe_2O_3. Weighed mixtures were wet milled in alcohol for 1 hr and heated to 1000°C for 15 hr. The pre-heated materials were milled once more, pressed to disks and fired for 2 to 18 hr in an electrical furnace. After the firing the disks were quenched, ground, and investigated with a Philips X-ray diffractometer using Co radiation.

Some physical properties were measured. These properties were: specific gravity (d), d.c. resistivity (ρ) magnetic saturation at room temperature in a field of 6000 oerstedt (σ).

RESULTS AND DISCUSSION OF THE RESULTS

The results of our investigation are collected in the Figs. 1 and 2. At the corners of the phase diagrams of the system $MgO—Fe_2O_3—Al_2O_3$, $FeO_{1·5}$ and $AlO_{1·5}$ are put instead of Fe_2O_3 and Al_2O_3. These formulae are chosen, because the Mg^{2+}, Al^{3+} and Fe^{3+} ions are of equal importance; the points in the diagrams immediately give the ion ratio. The diagram drawn in Fig. 1 gives the results of the firing at 1250°C in air, those in Fig. 2 the results of the firing at 1400°C in O_2. First, we briefly

* The analyses were carried out by Mr. J. VISSER in the Analytical Department of our laboratory.

[7] A. MUAN and C. L. GEE, *J. Amer. Ceram. Soc.* **39**, 207 (1956).
[8] G. O. JONES and F. F. ROBERTS, *Proc. Phys. Soc.* B **65**, 390 (1952).
[9] G. H. JONKER, Private communication.

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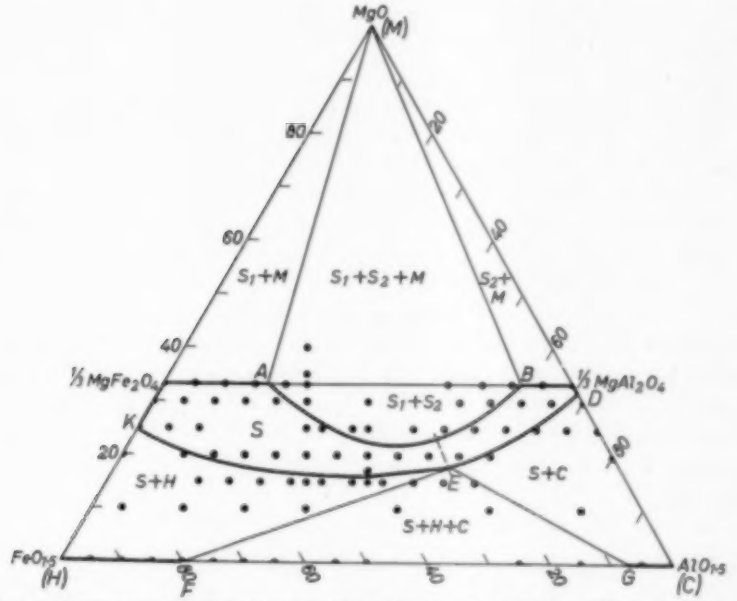

FIG. 1.—Diagram representing the system $MgO—Fe_2O_3—Al_2O_3$ fired at 1250°C. S = broad spinel band, S_1 = $MgFe_2O_4$(ss), S_2 = $MgAl_2O_4$(ss), H = Hematite (ss), C = corundum (ss) M = MgO. Thick lines represent one-phase areas. Samples of the spinel phase left of the broken line are ferrimagnetic at room temperature.

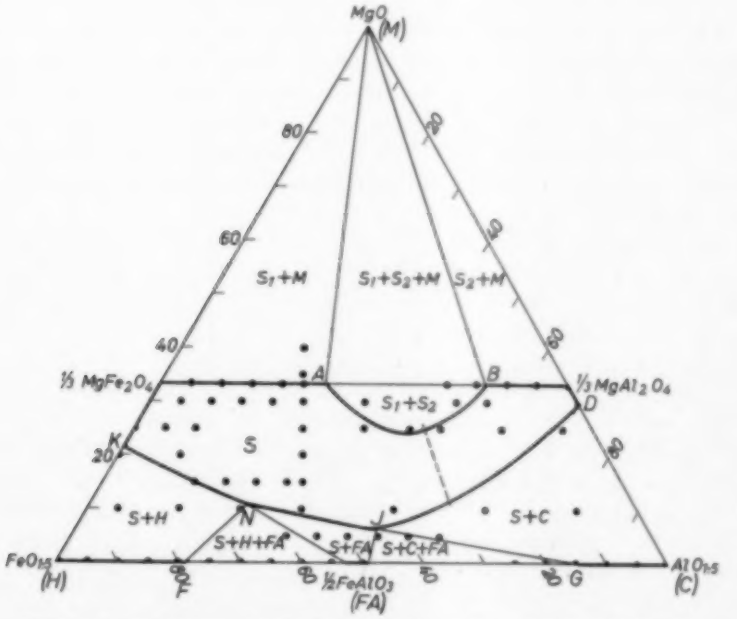

FIG. 2.—Diagram representing the system $MgO—Fe_2O_3—Al_2O_3$ fired at 1400°C. FA = $FeAlO_3$(ss), for other symbols, see Fig. 1.

review the two component system $MgFe_2O_4$—$MgAl_2O_4$ and afterwards discuss the ternary diagrams at 1250°C and 1400°C.

As mentioned in the introduction, only poor agreement is found in the literature data about the miscibility of the two spinel phases in the $MgFe_2O_4$—$MgAl_2O_4$ system. JONES and ROBERTS[8] found a complete series of mixed crystals. In our investigation, however, a miscibility gap was found, in agreement with the data of JONKER.[9] The discrepancies originate from the different firing and cooling techniques. GORTER[10a] describes the influence of firing temperature, duration of firing and quenching technique on the saturation magnetisation of $MgFe_2O_4$. The solubility of $MgFe_2O_4$—$MgAl_2O_4$ is also determined by these techniques. In our investigation the samples were quenched in a sand bath at room temperature.

It is possible to explain the occurrence of a miscibility gap by the difference in structure of $MgAl_2O_4$ and $MgFe_2O_4$ and, to a smaller degree, by the small difference in cell dimensions of both compounds (8·07 Å and 8·36 Å respectively). The structures of $MgAl_2O_4$ and $MgFe_2O_4$ are not identical: $MgAl_2O_4$ is a normal spinel, $MgFe_2O_4$ a more or less inverse spinel, depending on temperature. If $MgFe_2O_4$ is described as $Fe_{1-x}Mg_x[Mg_{1-x}Fe_{1+x}]O_4$,[10a] the distribution parameter x can be found from the temperature according to a distribution law given by NÉEL:[10b]

$$x(1 + x)/(1 - x)^2 = \exp(-E/kT)$$

with $E/k \sim 1220$°K. At room temperature $x = 0{\cdot}015$, at very high temperature $x = 0{\cdot}33$, so that $MgFe_2O_4$ goes from inverse to random structure. The miscibility gap, represented in Figs. 1 and 2 by AB, decreases as the temperature increases. At still higher temperatures, the solubility between both spinel phases may be complete and the results of JONES and ROBERTS may be found if the samples are well quenched.

Looking now at the ternary diagrams, the points k give the solubility limit of Fe_2O_3 in $MgFe_2O_4$. This solubility increases at increasing temperature. The solubility of Al_2O_3 in $MgAl_2O_4$ is represented by point D in Figs. 1 and 2. Our Al_2O_3-rich samples all reached a state of equilibrium very slowly, and so the positions of the points D are not very accurate. ROY *et al.*[4] give a higher value of the solubility limit of Al_2O_3 in $MgAl_2O_4$. As they investigated the composition of annealed spinel solid solutions formed during crystallization of fused mixtures of spinel and alumina, their values are more reliable.

Between the points $ABDK$ in Figs. 1 and 2 we have a broad spinel region, marked by an S. The first remarkable fact is the decreasing miscibility gap between $MgFe_2O_4$ and $MgAl_2O_4$ as the amount of $(Al, Fe)_2O_3$ in the spinel is increased. For both firing temperatures the miscibility gap disappears at 20–25 mole % MgO and so there is only one spinel phase. Another striking fact is the increasing solubility of sesquioxide in the spinel phase if a mixture of Fe_2O_3 and Al_2O_3 is present instead of one oxide only. This solubility reaches a maximum at about equal amounts Al_2O_3 and Fe_2O_3. Addition of Fe_2O_3 or Al_2O_3 over the stoicheiometric ratio increases the number of cation vacancies, giving an extra entropy term in addition to the entropy of mixing.

The formation of a solid solution will be more probable and the miscibility gap between the two spinel phases will become smaller and smaller as the number of cation vacancies increases. At 1250°C as well as at 1400°C we found such a stable one-phase area.

[10a] E. W. GORTER, *Phil. Mag. Supplement*, **23**, 336 (1957); [b] L. NÉEL, *C. R. Acad. Sci., Paris* **230**, 190 (1950).

An important difference between Figs. 1 and 2 is that at 1400°C the compound $FeAlO_3$ is present. According to MUAN and GEE,[7] this compound is formed at temperatures above 1318°C. Therefore the phase diagram at 1400°C is somewhat more complicated than that at 1250°C.

Samples with compositions like "hoegbomite"

In *Dana's System of Mineralogy* a mineral called "hoegbomite" with a hexagonal structure is mentioned.[11] The composition of this hoegbomite is $Mg(Al, Fe^{3+}, Ti)_4O_7$ with Al : Fe : Ti = 6 : 1 : 1. Optical methods showed the crystals to be anisotropic. According to a recent X-ray investigation of the mineral by MME. MICHEL-LÉVY and SANDRÉA[12] a hoegbomite, $(Fe, Mg)_6(Al, Fe)_{16}TiO_{32}$, had a tetragonal structure with $a = 8{\cdot}34$ Å and $b = 7{\cdot}96$ Å. The authors notice that this unit cell is closely related to the cubic spinel cell in which one Ti^{4+} replaces two (Mg, Fe). From our Figs. 1 and 2, one-phase spinel samples can be found with a large range of ratios Mg : (Al, Fe). So there is a large number of samples with a composition of hoegbomite minerals. By adding some TiO_2 to the spinel compositions, it is perhaps possible to obtain the tetragonal structure, but the results of firing at 1400°C are always a cubic spinel phase and a phase $(Fe, Al)_2TiO_5$. As many spinels become tetragonal at low temperature, some cubic spinel phases with hoegbomite composition were tempered at 1000°C However the spinel phase remained cubic, while some Fe_2O_3 appeared as a second phase. So the Ti^{4+} ions seem to be essential for the tetragonal hoegbomite structure and the TiO_2 may be absorbed in the spinel lattice at a temperature far above 1400°C

TABLE 1.—SOME PHYSICAL PROPERTIES OF SAMPLES FIRED AT 1200°C IN AIR. THE COMPOSITIONS IN THE SECOND COLUMN, ARE "MOLE %" MgO, $FeO_{1.5}$ OR $AlO_{1.5}$. σ = MAGNETIZATION AT 20°C, ρ = D.C. RESISTIVITY AND d = DENSITY

Sample number	MgO	$\frac{1}{2}Fe_2O_3$ (mole %)	$\frac{1}{2}Al_2O_3$	σ (gauss $cm^3\ g^{-1}$)	Log ρ (ρ in ohm cm)	d (g/cm^3)
472	30	70	—	24·3	7·1	4·20
473	30	65	5	25·4	7·3	4·11
474	30	60	10	22·3	7·1	4·95
477	25	75	—	22·1	7·0	4·18
478	25	70	5	28·8	6·7	4·25
479	25	65	10	26·5	6·9	4·02
406	20	70	10	31·5	7·2	4·00
452	20	65	15	26·7	7·6	4·09
407	20	60	20	23·6	8·2	3·96
453	20	55	25	19·3	7·1	3·86

Physical properties

In Tables 1 and 2, the results of some physical measurements are collected. The second column gives the composition of the samples. The third, fourth and fifth columns give the values of the saturation magnetization (σ) at 20°C, the logarithm

[11] *Dana's System of Mineralogy*, ref. (5), p. 723.
[12] MME. M. C. MICHEL-LÉVY and A. SANDRÉA, *Bull. Soc. Franç. Minér. Crist.* **76**, 430 (1953).

of the d.c. resistivity (log ρ) and the apparent density (d) respectively. From the tables we find that the saturation magnetization is increased if the Fe^{3+} ions and vacancies are substituted for the Mg^{2+} ions, as was found already in 1936 by SNOEK.[13] The saturation magnetization decreases if Al^{3+} is substituted for Fe^{3+} ions in the spinel phase, as was found by JONES and ROBERTS.[8] A survey of the work on the saturation

TABLE 2.—SOME PHYSICAL PROPERTIES OF SAMPLES FIRED AT 1400°C IN OXYGEN AT 1 ATM

Sample number	MgO	$\frac{1}{2}Fe_2O_3$ (mole %)	$\frac{1}{2}Al_2O_3$	σ (gauss cm^3 g^{-1})	Log ρ (ρ in ohm cm)	d (g/cm^3)
442	33⅓	66⅔	—	24·9	6·8	4·11
443	33⅓	61⅔	5	22·8	7·0	3·86
444	33⅓	56⅔	10	19·3	7·4	3·92
477	25	75	—	31·1	5·6	4·15
478	25	70	5	27·7	6·8	3·91
479	25	65	10	24·4	6·7	4·17
406	20	70	10	31·2	7·0	4·07
452	20	65	15	27·0	6·6	4·07
407	20	60	20	23·2	5·8	3·98
494	15	70	15	28·2	7·1	4·25
495	15	65	20	27·0	7·1	3·82
496	15	60	25	23·4	6·7	3·94
438	10	65	25	22·0	7·4	3·76

magnetization as a function of chemical composition is given by GORTER.[14] Log ρ has for all one-phase spinel samples a rather high value ($\sim$7). The Curie temperature varies in the same way as the magnetization. A broken line in both Figs. 1 and 2 indicates the sample compositions with a Curie temperature of about 20°C. Only on the left side of this line the samples are ferrimagnetic at room temperature.

Acknowledgements—The author wishes to express his thanks to Dr. G. H. JONKER for critical remarks. He wishes further to acknowledge the collaboration of Mr. J. VISSER who carried out the chemical analyses of some samples.

[13] J. L. SNOEK, *Physica* **3**, 463 (1936).
[14] E. W. GORTER, *Philips Res. Rep.* **9**, 429 (1954).

J. Inorg. Nucl. Chem., 1959, Vol. 9, pp. 71 to 81. Pergamon Press Ltd. Printed in Northern Ireland

THE MECHANISM OF RACEMIZATION OF THE TRIS (ETHYLENEDIAMINE)COBALT(III) CATION*

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(*Received* 26 *April* 1958)

Abstract—The tris(ethylenediamine)cobalt(III) cation, $[Co(en)_3]^{3+}$, has been shown to exhibit a racemization process in aqueous solution under forcing conditions, and the mechanism of the homogeneous racemization process has been investigated. It is postulated that the observed racemization process proceeds by an S_N2 collision mechanism: $[Co(en)_3]^{3+} + en \rightleftharpoons$ [primary intermediate or activated complex].

Above 70° and in the presence of 94 moles of unco-ordinated ethylenediamine per mole of complex ion, pseudo first-order kinetics are observed with an energy of activation over the temperature range 74° to 85° of 24·6 ± 0·5 kcal/mole. The rate of exchange of carbon-14-labelled ethylenediamine with the unlabelled complex is similar to that of the racemization process. Hydroxide ion can attack the complex ion at 85° to form an ethylenediamine-hydroxo complex ion. However, it appears that hydroxide ion does not play a key role in the overall racemization process. A periodic variation of the racemization with time is observed under certain concentration conditions.

THE tris(ethylenediamine)cobalt(III) cation, $[Co(en)_3]^{3+}$, has been previously reported to be an inert co-ordination complex that does not exhibit a racemization process in a homogeneous aqueous solution.[1] A heterogeneous catalysis of a racemization process of this complex using activated charcoal has been reported by DOUGLAS,[2] and a homogeneous catalysis based on the electron exchange of $[Co^{III}(en)_3]^{3+}$ with $[Co^{II}(en)_3]^{++}$ is under investigation by BUSCH[3] The present study has shown that under forcing conditions the tris(ethylenediamine)cobalt(III) cation undergoes a non-catalytic, homogeneous racemization process in aqueous solution, and the mechanism of this homogeneous racemization process has been investigated.

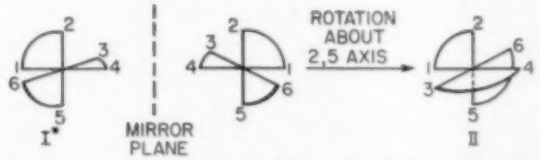

FIG. 1.—Mirror-image configurations of tris-bidentate metal-chelate complexes.

The individual enantiamorphs of the tris(ethylenediamine)cobalt(III) co-ordination complex can be conveniently represented by the structural formulas I and II, Fig. 1, where arabic numbers are used to distinguish the nitrogen atoms and the midpoint represents the cobalt(III) ion. The configurational interconversion of the two isomers which leads to racemization merely requires the interchange of the

* Based upon a portion of the doctoral dissertation of W. G. GEHMAN, The Pennsylvania State University (1954).

† Union Carbide Corporation Fellow, 1952–53.

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[1] A. WERNER, *Ber. Dtsch. Chem. Ges.* **45**, 121 (1912); F. BASOLO, *Chem. Rev.* **52**, 459–527 (1953).
[2] B. DOUGLAS, *J. Amer. Chem. Soc.* **76**, 1020 (1954).
[3] D. H. BUSCH, *J. Amer. Chem. Soc.* **77**, 2747 (1955).

"planes" of any two rings formed by the bidentate ligand and the metal ion. The numbe rof possible racemization mechanisms of tris-bidentate co-ordination complexes can be shown to be finite, and can be conveniently divided into four mechanism types: three S_N1 mechanisms involving the initial rupture of two, one, and zero co-ordinate bonds respectively, and a fourth S_N2 mechanism, involving the formation of a new co-ordinate bond. The primary intermediates of these different mechanisms would be respectively: $[Co(en)_2]^{3+}$; $[Co(en)_2(mono\text{-}en)]^{3+}$, where "mono-en" represents an ethylenediamine molecule acting as a monodentate ligand,[4] an activated trigonal-prism form of $[Co(en)_3]^{3+}$;[5] and $[Co(en)_3Y]^{(3+y)+}$, where Y represents an attacking group of charge y, and in the present case Y = (mono-en). Co-ordination complexes with the structures similar to the first three primary intermediates above have been reported by previous workers (cf. BASOLO[1]), but the last structure is postulated here for the first time. If stable electronic orbitals are available, and a fourth bidentate ligand co-ordinates as a monodentate group, the primary intermediate of the S_N2 collision mechanism is a seven-co-ordinate, tetrakis-bidentate co-ordination complex. However, in certain cases, one of the six original co-ordinate bonds might rupture simultaneously with the formation of the seventh bond, in which case the primary intermediate would be more properly termed an activated complex.

EXPERIMENTAL

1. *Preparation of* D-$[Co(en)_3]I_3 \cdot H_2O$. The compound $[Co(en)_3]Cl_3 \cdot 3H_2O$ was prepared by the method of WORK,[6] and resolved by the method of WERNER[1] which utilizes the chloro-*d*-tartrate salt. The diastereomer containing the dextro-rotatory complex cation is much less soluble than that containing the levorotatory cation. Treatment of the separated diastereomer, D-$[Co(en)_3]$(Cl, *d*-tartrate)$\cdot 5\ H_2O$, with excess KI yields the final product, D-$[Co(en)_3]I_3 \cdot H_2O$. The product exhibited a specific rotation of $+133{\cdot}3°$ with a sodium lamp, reported $+132°$. (Found: I, 59·79; 59·60. Calc. for $[Co(C_2N_2H_8)_3]I_3 \cdot H_2O$: I, 59·68%).

2. *Racemization studies*. The majority of the optical activity measurements were made with a Schmidt–Haensch double-field polarimeter; however, an O. Rudolph double-field polarimeter was used for experiment 9, Table 1, and three additional Experiments (1a, 1b and 1c) run under conditions similar to Experiment 1, Table 1, but at three different temperatures (79·5, 74·0 and 70·0°). Both instruments could be read to $\pm 0{\cdot}01°$, and, with only a few exceptions, each optical activity datum point represents the average of at least ten readings. Experiments 1–8, Table 1, were run at $85 \pm 0{\cdot}5°$ but the optical activities were read at room temperature, at which temperature no racemization occurred. The maximum error introduced into the per cent racemization at a given datum point, due to the time lags involved in the heating and quenching, was estimated to be 8, 4, and 2 per cent of the observed activity for 15, 30, and 60 min heating periods, respectively; and the majority of heating periods were of 60 min duration or longer. For these runs, the reaction flask was a 10 ml Erlenmeyer flask fitted with a reflux condenser to prevent loss by

* Species I shown to be D(+)—$[Co(en)_3]^{3+}$ by SAITO *et al.*[7]

[4] I. I. CHERNYAEV, *Ann. Inst. Platine (U.S.S.R.)* **4**, 243 (1926); I. I. CHERNYAEV and A. N. FEDOROVA, *Ibid.* **14**, 9 (1937); G. SCHWARZENBACH: *Helv. Chim. Acta* **35**, 2337 (1952).
[5] P. RAY and N. K. DUTT, *J. Indian Chem. Soc.* **20**, 81 (1943).
[6] J. B. WORK, *Inorg. Synth.* **2**, 221 (1946).
[7] Y. SAITO, K. NAKATSU, M. SHIRO and H. KUROYA, *Acta Cryst.* **8**, 729 (1955).

evaporation while heating since a decreasing volume would appear as an increasing optical activity. The solution was transferred to a 10 ml, 1 dm polarimeter tube for measurement. Experiments 1a, 1b, 1c and 9 were run in a 10 ml, 1-dm water-jacketed polarimeter tube closed with a tight-fitting rubber stopper; the temperatures

TABLE 1.—EXPERIMENTAL CONDITIONS OF THE RACEMIZATION EXPERIMENTS

Experiment	Ratio of components				pH	Remarks
	en	enH^+	$[Co(en)_3]^{3+}$*	OH^-†		
1	94	$\frac{1}{4}$	1	$\frac{1}{4}$	11·6	—
2	9·4	0	1	0	10·8	—
3	9·4	$\frac{1}{4}$	1	$\frac{1}{4}$	11·8	extra OH^- added
4	0	0	1	3	12·7	—
5	0	0	1	$\frac{1}{4}$	11·9	aged 24 hr.
6	0	0	1	$\frac{1}{4}$	11·9	run immediately
7	307	134	1	0	10·7	—
8	80	27	1	0	10·6	sinuous curves
9	88	3·2	1	$\frac{1}{4}$	11·5	sinuous curves

* The concentration of the complex ion was 0·0165 M for Experiments 1–8, and 0·0109 M for Experiment 9.

† Calculated from listed pH values and then rounded off.

were maintained within $\pm 0{\cdot}02°$. The optical activities are reported in terms of a per cent racemization, $\%R$, with respect to the optical activity at an arbitrarily selected zero time. The experimentally reported values of per cent racemization were calculated by the relation:

$$\%R = 100\,([\alpha]_i - [\alpha]_t)/[\alpha]_i$$

where $[\alpha]_i$ represents initial specific activities at the arbitrarily selected zero time of a given complete experiment, and $[\alpha]_t$ are the specific activities at time t. The conditions of the various racemization experiments are given in Table 1 and the data are plotted in Fig. 2. In addition, several experiments in which zero racemization was observed are mentioned in the "Discussion" section.

3. *Radioactive exchange experiments.* Carbon-14 labelled ethylenediamine dihydrochloride was synthesized by a method closely resembling that of POPPLEWELL and WILKINS.[8] The exchange reactions were run in the same fashion as the racemization Experiments 1–8 using a 10 ml Erlenmeyer flask fitted with a reflux condenser. The carbon-14 labelled ethylenediamine dihydrochloride was neutralized with a KOH solution* and added to an aqueous solution of unlabelled ethylenediamine and/or unlabelled complex, $[Co(en)_3]I_3 \cdot H_2O$. After standing for a given time at the desired temperature, the mixture was mixed with 10 ml of a saturated KI solution and set aside in ice. After a few hours, the iodide precipitate was separated by filtering through a piece of hard filter paper (Schleicher and Schuell No. 576), washed once with water, and dried first with suction and then in an oven at 110°. The activities were counted with a scaling unit made by the Nuclear Instrument and Chemical Corp. (model 165) and a Geiger–Müller counting tube with a 2·88 mg/cm²

* A very slight stoicheiometric deficiency of KOH was used so that the pH of the solution would be fixed by the free ethylenediamine alone.

[8] D. S. POPPLEWELL and R. G. WILKINS, *J. Chem. Soc.* 2521 (1955).

window thickness. All activities were corrected for self-absorption and background activity. The per cent exchange, $\%E$, Table 2, was calculated by the relation

$$\%E = 100 \cdot \frac{A_t}{A_\infty} = 100 \cdot \frac{A_t}{A_0 f(x/(x + y + 3z))}$$

where A_t = activity at time t
A_∞ = activity at infinite time
A_0 = specific activity of en*·2HCl, 13,000 counts/min per mg per cm²
f = gravimetric factor,
$3(\text{en}^*\cdot 2\text{HCl})/[\text{Co(en)}_3]\text{I}_3\cdot\text{H}_2\text{O} = 0{\cdot}625$
x = mmoles of en*·2HCl
y = mmoles of diluting en
z = mmoles of $[\text{Co(en)}_3]\text{I}_3\cdot\text{H}_2\text{O}$.

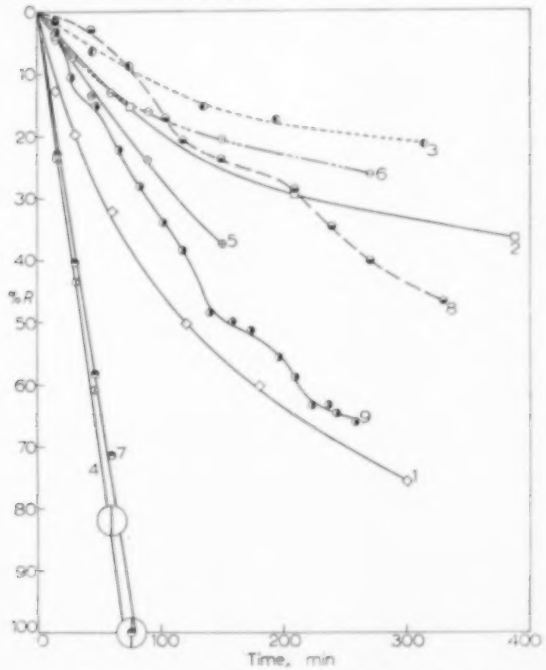

FIG. 2.—Racemization experiments (cf. Table 1).

The conditions and results of the radioactive exchange experiments are presented in Table 2.

TABLE 2.—RADIOACTIVE EXCHANGE EXPERIMENTS

Experiment	Mole ratio of components			Temp (°C)	Time (hr)	Exchange (%)
	en	en*	complex			
10	0	1	1	85	2	0
11a	90	2	1	85	2·5	39
11b	90	2	1	room temp.	2	1
12	90	2	1	85	5	47
WILKINS and POPPLEWELL[9]	0	0·2	1	100	6	0

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RESULTS AND DISCUSSION

Racemization and radioactive exchange experiments. The unimolecular S_N1 mechanisms are eliminated as possible routes of the racemization process by the great inertness of the tris(ethylenediamine)cobalt(III) cation reported by previous workers[1] and also observed in the following experiments (not listed in Table 1). Zero racemization of aqueous solutions of the complex ion is observed after: (1) 3 months at 25°, (2) 24 hr at 85°, (3) 15 hr in concentrated HCl (pH < 2) at reflux temperatures, (4) 75 min at 85° in the presence of a hundredfold excess of nitrite ion, and (5) 24 hr in the presence of either hydroxide ion (pH = 12·7) or 94 moles of ethylenediamine per mole of complex ion (pH = 11·9) at room temperature. Due to the improbability of distinct structural isomers having identical values of specific optical rotation, these results also eliminate the likelihood that the primary intermediate of either the dissociation mechanism, $[Co(en)_2]^{3+}$, or the intramolecular dissociation mechanism, $[Co(en)_2(mono\text{-}en)]^{3+}$, is formed and stabilized by the co-ordination of water molecules at the vacant sites.

Thus a simple process of elimination suggests that the S_N2 collision mechanism is operative in the observed racemization process. The first experimental verification of the S_N2 collision mechanism is found in the results of experiments 1 and 3, Fig. 2. Although no change in optical activity occurs over a 24 hr period at room temperature, at 85° racemization *does occur* in the presence of large excesses of unco-ordinated ethylenediamine. When the concentration of the ethylenediamine alone is reduced tenfold, the initial racemization rate[10] decreases tenfold. Thus the racemization rate exhibits a first order dependence upon the ethylenediamine concentration. Since the racemization rate will also have a first order dependence upon the concentration of the complex ion, the S_N2 character of the kinetics for the major portion of the racemization process is demonstrated.

A strong, direct dependence of the racemization rate on temperature is found in a set of experiments run to determine the energy of activation of the racemization process observed in the presence of a ninety-fourfold excess of free ethylenediamine per mole of complex ion. Despite the second order kinetics of the main racemization process, pseudo first order kinetics are observed in the presence of the large excess of ethylenediamine, Experiment 1. From the linear slopes of plots of time versus $\log_{10}[\alpha]_t$—not $\log_{10}$ (% racemization)—the racemization rate constant, k_R, in units of 10^{-3} min^{-1}, is found to have the value of 5·02, 2·97, and 1·68 at 85·0°, 79·5°, and 74·0° respectively, and a markedly decreased value of 0·69 at 70·0°. A plot of $\log_{10} k_R$ versus $1/T$(°K), Fig. 3, has a slope which is linear over the temperature range 85° to 74° and then drops off sharply between 74° and 70° (broken portion of curve) in correspondence with the sharp decrease in the value of k_R over the same temperature range. From the slope of the linear portion of the curve the energy of activation of the racemization process observed in the presence of the ninety-fourfold excess of ethylenediamine is calculated to be 24·6 $\pm$ 0·5 kcal/mole over the temperature range 74° to 85° which is not an untypical value for this type of reaction. Although the data do not permit any detailed, quantitative statements to be made, it is of interest to speculate about the reason for the sudden decrease in the activation energy from a very large (but undetermined) value that prevented any observable reaction at

[9] R. G. Wilkins and D. S. Popplewell, *Rec. Trav. Chim.* **75**, 815 (1956).
[10] K. J. Laidler, *Chemical Kinetics* pp. 14–18. McGraw-Hill, New York (1950).

room temperature to the value of 24·6 kcal/mole at 70°. Since steric hindrance is the greatest single factor in determining activation energies[11] it is reasonable to attribute the decrease in the activation energy to a decrease in the steric hindrance connected with the penetration of the ligand sheath about the cobalt(III) ion by a seventh —NH_2 group of a fourth ethylenediamine molecule in reaction (1) below.

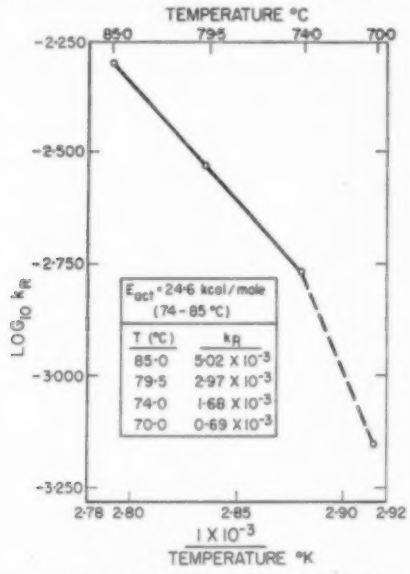

FIG. 3.—Plot of racemization rate constant vs. $1/T(°K)$.

Further experimental confirmation of the collision mechanism is provided by the radioactive exchange experiments, Table 2. Experiments 11a and 12 show that exchange *does occur* between carbon-14 labelled ethylenediamine and the unlabelled complex under the same conditions and at a rate of the same order of magnitude as the racemization process of Experiment 1. A direct dependence of the exchange rate upon the ethylenediamine concentration is demonstrated by the zero exchange observed in Experiment 10 at a low ethylenediamine concentration, in agreement with the observations of WILKINS and POPPLEWELL.[9] Finally, a direct dependence of the exchange rate on the temperature is shown by a comparison of Experiments 11a and 11b. The similarity in the rates, and in the dependency of both rates upon temperature and the ethylenediamine concentration suggests that both the racemization and exchange processes have the same mechanism.

Hydroxide decomposition experiments. Hydroxide ion does not attack the tris(ethylenediamine)cobalt(III) cation at room temperature as is evidenced by the zero loss of optical activity in Experiments 4 and 5 after standing 24 hr at room temperature prior to the run at 85°. But at 85° the attack is rapid and the optical activity of the complex ion is destroyed, Experiments 4 and 5, Fig. 2. However, it must be emphasized that the observed reaction is *not a racemization process but rather a decomposition process* in which a new species is formed: the bis(ethylenediamine)aquahydroxocobalt(III) cation. This decomposition process darkens the

[11] A. A. FROST and R. G. PEARSON, *Kinetics and Mechanism* p. 200. Wiley, New York (1953).

solution colour from light orange to a red colour. This colour caused a large error towards the end of Experiment 4 (last two readings) and forced an early end to Experiment 5. A comparison of the initial rates of Experiments 4 and 5 shows that the observed decomposition process is approximately first order with respect to the hydroxide ion concentration. Thus the data strongly suggest that second order kinetics hold for the hydroxide decomposition process as well as for the racemization process.

With the exception of Experiment 6, all solutions have been mixed and allowed to stand *at least* 24 hr prior to being run. Evidence of an "ageing" effect is found in Experiment 6 which had the identical composition as Experiment 5 but on being run *immediately after mixing* failed to show any colour indication of decomposition, and proceeds much more slowly than Experiment 5, Fig. 2. This "ageing" phenomenon can be explained in terms of the ion-association pair formed between the tris(ethylenediamine)cobalt(III) cation and the iodide anion[12] which must be allowed to come to equilibrium with all the reagents in the solution prior to making a run. Allowing the solutions to stand 24 hr at room temperature is sufficient to achieve the necessary equilibrium in the solutions studied in this investigation, but the effect of such an ageing process must be considered in mechanism studies of co-ordination complexes.

Postulated reaction mechanisms. It is postulated that both the racemization and radioactive exchange reactions proceed by identical S_N2 collision mechanisms with the initial step being the attack of the tris(ethylenediamine)cobalt(III) cation by a free ethylenediamine molecule. The overall reaction can be conveniently thought of as proceeding in four distinct steps, which can be arranged in a logical sequence as represented by equations (1) to (4) below, but which may occur simultaneously in a given case. It is further postulated that the hydroxide decomposition reaction proceeds by a similar mechanism in which the first three steps are identical to those above except for the fact that the attacking group is now a hydroxide ion. The attacking group is written as Y^y which stands for either ethylenediamine, charge $y = 0$, or hydroxide ion, charge $y = -1$, whichever is appropriate.

The first step in this logical sequence is considered to be the formation of a reactive, seven-co-ordinate intermediate with a $3d^2 4s 4p^3 4d$ electronic configuration involving a mixture of inner and outer d orbitals,[13] equation (1).

$$[Co(en)_3]^{3+} + Y^y \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Co(en)_3Y]^{(3+y)+} \qquad (1)$$

The stereochemistry of compounds involving co-ordination number seven has recently been reviewed by O'BRIEN.[14] He notes that a face-centred octahedral configuration has been proposed for the inner-orbital d^3sp^3 hybrid[15] whereas a pentagol bipyramidal configuration has been proposed for the outer-orbital sp^3d^3 hybrid.[16] In light of the different configurations proposed for the inner- and outer-orbital hybrids, a theoretical analysis of the stereochemistry of mixed inner-outer-orbital hybrids would be of interest. Such a seven-co-ordinate cobalt(III) complex would in all probability be very unstable due to the fact that the electronic configuration of lowest energy involves the use of a high energy outer $4d$ orbital, and also due

[12] M. G. EVANS and G. H. NANCOLLAS, *Trans. Faraday Soc.* **49**, 363 (1953).
[13] H. TAUBE, *Chem. Rev.* **50**, 69–126 (1952).
[14] T. D. O'BRIEN, *Chemistry of the Coordination Compounds* (Edited by J. C. BAILAR) pp. 392–394. Reinhold, New York (1956).
[15] G. KIMBALL, *J. Chem. Phys.* **8**, 188 (1940).
[16] G. H. DUFFEY, *J. Chem. Phys.* **18**, 943 (1950).

to the high steric hindrance since the cobalt(III) ion is much smaller than the relatively large ions for which co-ordination number seven has been reported.[14] Due to the probable instability of a seven-co-ordinate cobalt(III) complex, it is postulated that the second step of the logical sequence of events is a very fast, irreversible rearrangement reaction involving the rupture of one cobalt–nitrogen co-ordinate bond and the formation of a six-co-ordinate intermediate, equation (2).

$$[Co(en)_3Y]^{(3+y)+} \xrightarrow{k_2} [Co(en)_2(\text{mono-en})Y]^{(3+y)+}. \qquad (2)$$

It is at this second step that the major part of the optical inversion occurs; the succeeding steps (3) and (4) mainly being required to regenerate the original complex ion. Hence, to a first approximation, reactions (1) and (2) can be combined and considered as the rate determining step of the overall racemization process and the observed rate constant, k_R, can be set equal to the equilibrium constant of reaction (1) times k_2, or k_1k_2/k_{-1}. This simplification is only approximate since a detailed analysis[17] shows that reaction (2) can lead to a complicated mixture of products which exhibit both retention and inversion of configuration depending upon which co-ordinate bond of the primary intermediate ruptures. The probability of rupture of the different, individual co-ordinate bonds would of course depend upon the structure of the primary intermediate, and it is interesting to note that both possibilities, i.e. the face-centred octahedron and the pentagonal bipyramid, have two structural isomers. In the former case, the seventh amine group could bond at either one of a set of two triangular faces perpendicular to the threefold rotation axis of the octahedron, e.g. face 246, Fig. 1, or at one of a set of six faces skewed to this rotation axis, e.g. face 234. In the latter case, the monodentate ethylenediamine could bond at either an apical or an equatorial position of the pentagonal bipyramid.

In order for either the racemization (and the exchange) reaction or the hydroxide decomposition reaction to proceed to completion by the formation of the tris-(ethylenediamine) cobalt (III) and the bis (ethylenediamine) aquahydroxocobalt (III) complexes, respectively, it is necessary that one of the six co-ordination bonds of the $[Co(en)_2(\text{mono-en})Y]^{(3+y)+}$ species ruptures. For this reason, the dissociation of a monodentate ethylenediamine ligand to form a reactive, five-co-ordinate intermediate is postulated to be a third step of the logical sequence of events common to the racemization, exchange, and hydroxide decomposition reactions, equation (3).

$$[Co(en)_2(\text{mono-en})Y]^{(3+y)+} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} [Co(en)_2Y]^{(3+y)+} + \text{en}. \qquad (3)$$

This five-co-ordinate species which is identical to the primary intermediate postulated for the S_N1 intramolecular dissociation mechanism (which was eliminated from consideration above) would be expected to be very reactive and undergo further co-ordination by either water molecules or hydroxide ion. In order to explain the observation of racemization without decomposition, it is necessary to differentiate between the mechanism of the racemization and exchange reactions and that of the hydroxide decomposition reaction at this point. In the racemization and exchange reactions, in which case Y = en in equations (1) through (3) above, the final step is postulated to be very fast, irreversible ring-closure reaction. In this step the reactive,

[17] W. G. GEHMAN, Thesis, Pennsylvania State Univ. (1954).

five-co-ordinate product of equation (3) is converted to the original tris(ethylenediamine)cobalt(III) cation as in equation (4).

$$[Co(en)_2(mono\text{-}en)]^{3+} \xrightarrow{k_4} [Co(en)_3]^{3+}. \quad (4)$$

Thus the five-co-ordinate intermediate is removed from the reaction zone as fast as it is formed. In contrast, the final step of the hydroxide decomposition reaction, in which case $Y = OH^-$ in equations (1) through (3), is postulated to be an equilibrium aquation reaction in which the reactive, five-co-ordinate intermediate is converted to the bis(ethylenediamine)aquahydroxocobalt(III) cation as in equation (5).

$$[Co(en)_2(OH^-)]^{2+} + H_2O \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} [Co(en)_2(OH^-)H_2O]^{2+}. \quad (5)$$

The forward rate of a direct hydroxide attack on $[Co(en)_2(mono\text{-}en)]^{3+}$ would necessarily be slower than that of reaction (4) since a hydroxide ion must diffuse through the solvent and co-ordinate at the vacant site.

The role of hydroxide ion in the racemization process. Aqueous solutions of ethylenediamine necessarily contain hydroxide ion which the present work shows will attack the tris(ethylenediamine)cobalt(III) cation under the temperature and pH conditions of the racemization process. Therefore, the question arises whether hydroxide ion is essential or merely incidental to the racemization reaction observed in the presence of excess ethylenediamine. To answer this question, three possible mechanisms which differ from the postulated racemization mechanism have to be examined in terms of the present data.

The first case is an S_N1 mechanism that differs from the S_N1 mechanisms already eliminated in that the initial step is a proton abstraction reaction. This type of mechanism was originally proposed by GARRICK[18] and can be termed an S_N1CB mechanism, where *CB* stands for "conjugate base"[19] or $[Co(en)_2(H_2NC_2H_4NH^-)]^{++}$ in the present case. The rate determining step of this alternate mechanism would be expected to be the dissociation of an amine nitrogen atom from the cobalt(III) ion to form a symmetrical, trigonal-bipyramidal intermediate that is stabilized by π-bonding between the amido nitrogen and the cobalt(III) ion.[19] Since racemization would in effect have occurred with the formation of the symmetrical intermediate, the rate of this reaction would be independent of the ethylenediamine concentration in disagreement with the observed data. Moreover, in Experiments (2) and (3), Fig. 2, an increase in the hydroxide ion concentration alone causes a decrease in the observed racemization rate. Although it is possible for the rate of a reaction proceeding by an S_N1CB mechanism to be independent of the hydroxide ion concentration, an inverse dependence cannot be explained by this mechanism. Therefore, the racemization of the tris(ethylenediamine)cobalt(III) cation cannot be explained in terms of an S_N1CB mechanism.

The second case poses a more serious problem in view of the racemization mechanism postulated above. This possibility involves an exchange of hydroxide and ethylenediamine groups by a displacement reaction[20] occurring as a sequel to reaction (2) of the postulated mechanism with $Y = OH^-$ originally, as represented by equation (6).

$$[Co(en_2(mono\text{-}en)(OH^-)]^{2+} + en \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} [Co(en)_2(mono\text{-}en)_2]^{3+} + OH^-. \quad (6)$$

[18] F. J. GARRICK, *Trans. Faraday Soc.* **34**, 507 (1937).
[19] R. G. PEARSON and F. BASOLO, *J. Amer. Chem. Soc.* **78**, 4878–4883 (1956).
[20] L. P. HAMMETT, *Physical Organic Chemistry* Chap. V. McGraw-Hill, New York (1940).

This question can be settled by comparing the results of the last three sets of experiments, Fig. 2: (a) Experiments 5, 3, and 1; (b) Experiments 3 and 2; and (c) Experiments 7, 8, and 9.

Experiments 5, 3, and 1 have similar hydroxide ion concentrations, but dissimilar concentrations of unco-ordinated ethylenediamine per mole of complex ion (0, 9·4, and 94 moles). The decrease in rate in going from the pure hydroxide decomposition reaction of Experiment 5 to the conditions of Experiment 3 can be interpreted as a shift of the equilibrium of reaction (3) to the left by the excess ethylenediamine. Although such a shift of this equilibrium would have a large effect on the rate of loss of optical activity by the hydroxide decomposition reaction, it would not be expected to have a large effect on the rate of racemization without decomposition. This situation which seems contradictory at first arises since the very fast, last step of the racemization process, equation (4), does not require that the monodentate ethylenediamine ligand which has ruptured its co-ordinate bond to the cobalt(III) cation diffuse away through the cage of surrounding solvent molecules. Instead, this fast reaction can occur immediately upon the vacation of the co-ordination position of the dissociated monodentate ethylenediamine ligand. Therefore, it appears likely that the increased rate in going from Experiment 3 to 1 is at least partially, if not wholly, due to the direct attack of the original complex ion by ethylenediamine as in equation (1) rather than by the displacement reaction (6). This supposition is confirmed by a comparison of Experiments 3 and 2. The increase in rate with decrease in hydroxide ion concentration taken in conjunction with Experiments 5, 3 and 1 shows that the racemization and hydroxide decomposition reactions are essentially two separate, simultaneous reactions and that the total loss of optical activity is the sum of the loss due to both reactions occurring at once.

Final confirmation that the racemization and hydroxide decomposition reactions are not consecutive reactions in which the hydroxide attack precedes the ethylenediamine attack, but rather are simultaneous reactions, is found in Experiments 7, 8, and 9. The hydroxide ion concentration in this last set of experiments is reduced by buffering the solutions with ethylenediamine monohydrochloride. The cationic species $H_2NC_2H_3NH_3^+$ appears to play no role other than reducing the hydroxide concentration since zero racemization is observed when a solution containing 100 moles of ethylenediamine monohydrochloride per mole of complex ion is heated at 85° for 2 hr. Experiment 7, in which the hydroxide concentration is less than that of Experiment 4, shows that *hydroxide ion is not essential to the occurrence of a very rapid racemization reaction.* Due to the extremely high concentration of neutral ethylenediamine the rate is the same as the very rapid hydroxide decomposition reaction of Experiment 4, but no decomposition coloration is observed.

In Experiments 8 and 9, periodic variations of the racemization rate with time are observed. This is the second reported case of a periodic reaction occurring in a homogeneous liquid solution; the first was reported by BRAY in 1921 for the H_2O_2—I_2—HIO_3 system.[21] In accordance with a mathematical analysis by LOTKA,[22] BRAY suggested that his results could be interpreted on the basis of an autocatalytic step occurring in a series of consecutive reactions. In the present case, since a

[21] W. C. BRAY, *J. Amer. Chem. Soc.* **43**, 1262 (1921).
[22] A. J. LOTKA, *J. Phys. Chem.* **14**, 271 (1910); reprinted *Z. Physik. Chem.* **72**, 508 (1910); *J. Amer. Chem. Soc.* **42**, 1595 (1920).

detailed analysis[17] has shown that a complicated series of simultaneous and consecutive reactions would be expected in the racemization process, the periodicity can be interpreted in terms of a mutarotation reaction in which the new species has a specific optical activity equal to or greater than that of the original species.

The third and final alternate mechanism to be considered stems from the suggestion by BUSCH[3] that the formation of a small amount of the reduced complex, $[Co^{II}(en)_3]^{2+}$, would catalyse the racemization of the tripositive species since the dipositive complex is a labile co-ordination complex. LEWIS and co-workers have studied the electronic exchange reaction between the di- and tri-positive species,[23] and report a rapid oxidation of the dipositive complex by traces of air at 25° and 45°, an energy of activation of 12·75 to 15·75 kcal/mole, but did not mention any effect of free ethylenediamine. Since the racemization process observed in this work had an energy of activation of 24·6 kcal/mole over the range 74° to 85° in an oxidizing atmosphere, required temperatures of at least 70°, and was directly dependent upon the ethylenediamine concentration, it does not seem likely that the catalytic racemization mechanism was operative in the present case.

Acknowledgements—This study was supported in part by the United States Atomic Energy Commission through Contract At(30–1)–907. The authors wish to express their appreciation to the Chemistry Department of the University of California at Riverside for permission to use their facilities to run a few supplemental experiments.

[23] W. B. LEWIS, C. D. CORYELL and J. W. IRVINE, JR., *J. Chem. Soc.* Supplement Issue No. 2, pp. S386–S329 (1949).

J. Inorg. Nucl. Chem., 1959, Vol. 9. pp. 82 to 85. Pergamon Press Ltd. Printed in Northern Ireland.

OBSERVATIONS ON THE RARE EARTHS—LXVIII[1]

PARTIAL RESOLUTION OF YTTRIUM AND GADOLINIUM ACETYLACETONATES BY MEANS OF A CHROMATOGRAPHIC TECHNIQUE

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Abstract—Adsorption of yttrium or gadolinium acetylacetonate on columns of D-lactose hydrate or D-lactose, followed by elution with benzene–petroleum ether, effects partial resolution of the chelates into optically active fractions. Racemization is slow and first order. Resolution of these ionically-bonded inner complexes suggests that the conditions employed are of controlling importance rather than the nature of the bonding.

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ISOLATABLE rare earth metal complexes that maintain their identities in solution appear to be limited to species derived from strongly chelating groups.[2] Similarities between the absorption spectra of solutions containing such complexes and solutions containing the uncomplexed (but solvated) cations[1,3–7] and identities of magnetic moments between typical diaminepolycarboxylic acid chelates and the corresponding 8-hydrated sulphates[7] suggest strongly that bonding in these species does not involve the 4*f* electrons. This is consistent with the view[8] that the 4*f* orbitals have shrunk sufficiently in the rare earth series that they are spatially unavailable for bonding. It is probable, therefore, that in a rare earth metal complex only relatively easily ionizable 5*d*, 6*s*, 6*p*, etc., orbitals can be employed, or that the bonding is largely ionic. The marked similarities between yttrium complexes and those of the rare earth metals suggest predominantly ionic bonding in these species as well, although it is reasonable to expect some reduction in ionic character because of use of the somewhat less easily ionizable 4*d*, 5*s*, and 5*p* orbitals. Such chemical characteristics as general lability in solution are in overall accord with this ionic picture.

The stereochemistry of these materials is thus of particular interest. Where potential asymmetry exists in the solid state, ionic bonding might be expected to lead to such rapid rearrangement of ligands in solution that resolution would be unlikely or impossible.[9] However, the polarity of the solvent should be considered also since the more polar the solvent the more labile the ligands in question. This suggests that although resolution in aqueous (or similar) medium would be unlikely, it might be effected in less polar solvents such as the hydrocarbons. Such a conclusion is supported by failure to resolve the relatively stable[10] ethylenediaminetetraacetate chelates,

[1] For the preceding paper in this series, see T. MOELLER and W. F. ULRICH, *J. Inorg. Nucl. Chem.* **2**, 164 (1956).
[2] T. MOELLER, *Record Chem. Progr.* **14**, 69 (1953).
[3] T. MOELLER and J. C. BRANTLEY, *J. Amer. Chem. Soc.* **72**, 5447 (1950).
[4] F. A. J. MOSS, Doctoral dissertation, University of Illinois (1952).
[5] R. C. VICKERY, *J. Chem. Soc.* 421 (1952); 385 (1954).
[6] L. HOLLECK and D. ECKHARDT, *Z. Naturf.* **8a**, 660 (1953); **9a**, 347 (1954); **9b**, 274 (1954).
[7] E. P. HORWITZ, Doctoral dissertation, University of Illinois (1957).
[8] R. M. DIAMOND, K. STREET, JR. and G. T. SEABORG, *J. Amer. Chem. Soc.* **76**, 1461 (1954).
[9] C. H. JOHNSON, *Trans. Faraday Soc.* **28**, 845 (1932).
[10] G. SCHWARZENBACH, R. GUT and G. ANDEREGG, *Helv. Chim. Acta* **37**, 937 (1954).

$[Ln(enta)(H_2O)]^-$ (Ln = yttrium or rare earth metal), by fractional crystallization of potential diastereoisomers[11] from aqueous medium as contrasted with the success reported herein for the resolution of the somewhat less stable[12] acetylacetone chelates in chloroform and hydrocarbon media. This suggests that environment may be a better criterion of resolvability than bond type.

The 1,3-diketone chelates in general combine well the essential properties of potential asymmetry and large solubility in non-polar media. The present study involves an extension of the chromatographic technique previously described[13] to yttrium and gadolinium acetylacetonates as typical chelates that also contain cations free from absorption bands that might complicate polarimeter readings. Chloroform and benzene–petroleum ether were studied as media of differing polarity.

EXPERIMENTAL

Materials. As previously outlined,[13] Merck U.S.P. or B. and A. Reagent Grade D-lactose hydrate, screened to −100 mesh, was used without further purification. For some runs, this material was dehydrated by heating at 125–130° for 3 hr. The D-quartz was obtained in −140 to +200 mesh size by grinding a large active crystal. All solvents were C.P. grade. Chloroform was freed from ethanol by shaking repeatedly with 18 M sulphuric acid. It was then washed with water, dried over potassium carbonate, and distilled. The fraction boiling at 61·0–61·5° was stored in brown bottles and used within 24 hr after distillation. Benzene was dried over sodium wire. Low-boiling petroleum ether was dried over anhydrous magnesium perchlorate and filtered just prior to use.

Yttrium and gadolinium acetylacetonates were prepared from 99 per cent pure oxides by variants[1] of the procedure of STITES *et al.*[14] Recrystallization was from dry benzene. The yttrium chelate melted at 131–133°: (Found: C, 43·30; H, 5·92; Y_2O_3, 28·88 Calc. for $Y(C_5H_7O_2)_3$: C, 46·64; H, 5·48; Y_2O_3, 29·24%). The gadolinium chelate melted at 145°: (Found: C, 36·27; H, 4·94; Gd_2O_3, 38·40. Calc. for $Gd(C_5H_7O_2)_3 \cdot H_2O$: C, 38.15; H, 4·91; Gd_2O_3, 38·31%).

Procedure. The column and general procedure were the same as previously described.[13] Breakthrough of solute was established by the orange-red colour developed on a spot plate with ethanolic iron(III) chloride. All optical measurements were made at 5893 Å with a Schmidt and Haensch polarimeter (No. 9143) calibrated to 0·001°. Readings were reproducible to ±0·003°. An average of ten readings was used for each sample, and blank readings were made before and after each sample was observed. Readings on solvent which had passed through the column before the latter was treated with the chelates were identical with the blanks. The quantity of chelate eluted was determined for each sample by evaporation and weighing. Eluted samples were micro-analysed to confirm identity between adsorbed and eluted chelate. Racemization was followed at 23–26° by periodic polarimeter readings.

RESULTS AND DISCUSSION

Data summarized in Tables 1 and 2 indicate at least partial resolution of the yttrium and gadolinium compounds with D-lactose hydrate or D-lactose as adsorbent.

[11] T. MOELLER, F. A. J. MOSS and R. H. MARSHALL, *J. Amer. Chem. Soc.* **77**, 3182 (1955).
[12] R. M. IZATT, W. C. FERNELIUS, C. G. HASS, JR. and B. P. BLOCK, *J. Phys. Chem.* **59**, 170 (1955).
[13] T. MOELLER and E. GULYAS, *J. Inorg. Nucl. Chem.* **5**, 245 (1958).
[14] J. G. STITES, C. N. MCCARTY and L. L. QUILL, *J. Amer. Chem. Soc.* **70**, 3142 (1948).

TABLE 1.—CHROMATOGRAPHIC DATA FOR ADSORPTION AND ELUTION OF YTTRIUM ACETYLACETONATE

Run	Solute adsorbed (g)	Solvent and eluant	Chromatographic conditions	Active eluted fractions		
				Volume (ml)	Solute (g)	Specific rotation $[\alpha]^*_{5893}$
Y(II)	1·5000	Chloroform	D-lactose hydrate 90 cm column 12 drops/min Breakthrough: 5 2/3 hr	22·5	0·463	+1·1
Y(III)	0·6160	Benzene	D-quartz 15 cm column	7	—	0
			7 ml/hr	7	—	0
			Breakthrough: 4 hr	7	—	0
			Total: 14 hr			
Y(IV)	1·0600	Benzene–petroleum ether (1 : 1)	D-lactose hydrate 90 cm column 20 ml/hr Breakthrough: 4 1/2 hr Total time: 8 hr	9	0·1810	−3·6
				8	0·1755	−3·0
				10	0·1949	−2·1
Y(VII)	1·000	Benzene–petroleum ether (1 : 1)	D-lactose 91 cm column 15 ml/hr Breakthrough: 7 1/2 hr Total time: 14 hr	13·5	0·3336	+3·5
				11	0·2537	+3·3
				22·5	0·0601	0

* Specific rotation, $[\alpha]_\lambda$, is calculated from the relationship

$$[\alpha]_\lambda = av/lw$$

Where a is the observed rotation in degrees, v is the total volume in ml, l is the length of the polarimeter tube in decimeters, and w is the weight of solute in grammes.

TABLE 2.—CHROMATOGRAPHIC DATA FOR ADSORPTION AND ELUTION OF GADOLINIUM ACETYLACETONATE

Run	Solute adsorbed (g)	Solvent and eluant	Chromatographic conditions	Active eluate fractions		
				Volume (ml)	Solute (g)	Specific rotation $[\alpha]_{5893}$
Gd(I)	0·2860	Benzene–petroleum ether (1 : 1)	D-lactose hydrate 91 cm column 20 drops/min Breakthrough: 6 hr	18	0·0391	−5
				20	0·0903	−3
				25	0·0379	0
Gd(II)	1·0000	Benzene–petroleum ether (1 : 1)	D-lactose 90 cm column 20 ml/hr Breakthrough: 5 1/2 hr Total time: 11 hr	15	0·1527	−6·0
				10	0·1948	−5·1
				11	0·2058	−3·0
				—	0·1100	0
Gd(III)	0·7160	Benzene–petroleum ether (1 : 1)	D-lactose 90 cm column 9 drops/min Breakthrough: 8 hr Total time: 15 hr	14	0·1203	−6·0
				12	0·1940	−4·3
				10·5	0·1492	−2·7
				12·5	0·0722	0

This is believed to be the first recorded resolution of an yttrium or rare earth metal compex. No evidence of resolution with D-quartz could be obtained.

The hydrated and anhydrous forms of D-lactose appeared to be equally effective. However, solutions treated with the former often became cloudy, apparently because of hydrolysis.[15] Use of the anhydrous adsorbent and rigorous drying of all reagents eliminated this difficulty and is recommended. It is of interest that with the yttrium

TABLE 3.—RACEMIZATION OF YTTRIUM AND GADOLINIUM ACETYLACETONATES IN 1 : 1 BENZENE–PETROLEUM ETHER

Sample	Time (hr)	Observed rotation (degrees)	Sample	Time (hr)	Observed rotation (degrees)
Y(VII)	0	+0·053	Gd(II)	0	−0·046
(first fraction)	3·58	+0·048	(second fraction)	6·5	−0·042
	17·67	+0·042		20	−0·036
	25	+0·023		96	−0·009
	38	+0·009		144	0·000
	47	0·000			
			Gd(III)	0	−0·033
			(first fraction)	3	−0·030
				20	−0·016
				36	−0·005
				44	−0·003

chelate the enantiomorph preferentially adsorbed varied with both eluting solvent and adsorbent. Such a change with change in chromatographic conditions has been noted in other systems.[16] No changes were noted with the gadolinium chelate, however. Maximum molecular rotations obtained were −1400° for the yttrium compound and −2700° for the gadolinium compound.

Although resolution of the yttrium chelate was effected in chloroform, it was difficult to obtain reproducible results, racemization was always rapid, and yellow bands often appeared on the columns.[17,18] It is probable that the higher polarity of chloroform and especially of its decomposition products contributed to lack of optical stability and probable decomposition of solute. In the absence of moisture, however, solutions in benzene–petroleum ether were chemically stable and racemized only very slowly. Racemization data in Table 3 indicate rough linearity between log [α] and time, in accordance with first-order kinetics. The process is being investigated more exactly.

These data are consistent with the conclusion that ionic bonding does not preclude resolution into optical isomers if conditions are so chosen that the lability associated with this type of bond is sufficiently suppressed.

[15] E. O. BRIMM, Doctoral dissertation, University of Illinois (1940).
[16] L. ZECHMEISTER, *Progress in Chromatography*, 1938–1947. Wiley, New York (1950).
[17] R. H. MARSHALL, Doctoral dissertation, University of Illinois (1954).
[18] E. GULYAS, Doctoral dissertation, University of Illinois (1955).

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SOME METHYL*CYCLO*PENTADIENYL–METAL COMPOUNDS

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Abstract—The preparation and properties of *bis*methyl*cyclo*pentadienyl derivatives of Fe, Ni, Ti, Zr, methyl*cyclo*pentadienides of Mn, Nd, and Tl, and methyl*cyclo*pentadienyl carbonyls of Mo, Mn and Fe are described. Manganese methyl*cyclo*pentadienide shows unusual magnetic behaviour, with co-operative effects that persist in the melt.

THE commercial availability of methyl*cyclo*pentadiene dimer permits the convenient preparation of various methyl*cyclo*pentadienyl compounds of transitional metals by methods entirely analogous to those used for the simple *cyclo*pentadienyl metal compounds.[1a,b] The unsubstituted derivatives of the compounds noted herein have been described previously. The main interest in making the methyl analogues was to check certain physical properties of the derivatives, notably the infra-red spectra of carbonyl derivatives and the magnetic properties of manganese methyl*cyclo*pentadienide.

Generally, the methyl*cyclo*pentadienyl–metal compounds melt 50–150° lower than the *cyclo*pentadienyl compounds. Crystal habits (and presumably structures) are different; the methyl compounds often crystallize in thin leaflets while the *cyclo*pentadienyls occur as prisms. Unless exceedingly great care is taken in purification of methyl*cyclo*pentadiene monomer, the metal products are often difficult to obtain as crystals and some tend to form viscous liquids. The methyl compounds are all much more sensitive to air oxidation than the *cyclo*pentadienyls.

The lower value of the polarographic half-wave potential for the reaction in 90% ethanolic electrolyte :

$$(CH_3C_5H_4)_2Fe \rightleftarrows (CH_3C_5H_4)_2Fe^+ + e$$

of +0·38 V vs. SCE as compared to that of ferrocene, +0·31,[2] is due to increased electron density on the rings and metal atom attributable to the methyl groups. This effect is also shown by the fact that the methyl*cyclo*pentadienyl anion is a stronger Brønsted base than the *cyclo*pentadienyl anion, as evidenced by the very slow reaction of methyl*cyclo*pentadiene with ethylmagnesium bromide, whereas *cyclo*pentadiene reacts rapidly.

A comparison of the infra-red spectra of the binuclear carbonyls $[C_5H_5Fe(CO)_2]_2$, $[C_5H_5Mo(CO)_3]_2$ and $C_5H_5Mn(CO)_3$ with the methyl analogues was of interest. It was found that replacement of a C_5H_5 group, with C_5 symmetry, by a $CH_3{\cdot}C_5H_4$

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[1a] G. WILKINSON, J. M. BIRMINGHAM and F. A. COTTON, *J. Inorg. Nucl. Chem.* **2**, 95 (1956); [b] T. S. PIPER, F. A. COTTON and G. WILKINSON, *J. Inorg. Nucl. Chem.* **1**, 165 (1955).
[2] J. A. PAGE and G. WILKINSON, *J. Amer. Chem. Soc.* **74**, 6149 (1952).

group of low symmetry produces no change in the spectrum in the C–O stretching region. This is in keeping with the view that the number of infra-red active modes is in accord with the local symmetry of the $M(CO)_x$ part of the molecules,[3] even though the molecule as a whole may possess virtually no symmetry.

The manganese methyl*cyclo*pentadienide has chemical behaviour similar to that of the *cyclo*pentadienide.[1a] Its magnetic behaviour is similarly anomalous, but has additional anomalies of its own at present unexplained. The data are given in Table 1 and Figs. 1 and 2.

TABLE 1.—MAGNETIC SUSCEPTIBILITY OF MANGANESE METHYL*cyclo*PENTADIENIDE

State	Temp. (°K)	$10^6\chi_g$	$10^6\chi_{mol}^{corr}$ [b]	μ_{eff}, B.M.
Crystalline solid[a]	196	40·3	8700	3·71
	225	38·7	8360	3·89
	245	37·9	8190	4·02
	273	36·3	7830	4·12
	300	35·3	7630	4·30
	315	34·5	7470	4·36
	320	34·4	7440	4·38
	328	34·0	7360	4·41
Liquid	305	38·6	8340	4·53
	329	39·8	8590	4·78
	335	39·9	8600	4·82
	355	39·5	8530	4·93
	365	38·9	8400	4·97
0·415 M Solution in tetrahydrofuran	195	103·3	22130	5·83
	222	88·2	18920	5·85
	245	81·3	16940	5·80
	273	72·2	15510	5·82
	300	65·3	14040	5·90

[a] Melting point 334–336°K.
[b] Formula weight 213·2; diamagnetic correction = 110×10^{-6} cgs units for C_6H_7 rings.

Crystalline manganese methyl*cyclo*pentadienide behaves very much like the brown form of manganese *cyclo*pentadienide, whose antiferromagnetism[1] and essentially ionic nature has been recently confirmed by paramagnetic resonance absorption studies.[4] Thus it has virtually the same Curie ($c = 6{\cdot}40$) and Weiss ($\theta = 540°$ vs. 492°) constants. A Néel temperature for the methyl*cyclo*pentadienide could not be determined under the present circumstances. Manganese methyl*cyclo*pentadienide shows no obvious phase transition below its melting point. At the melting point there is a discontinuity in its magnetic susceptibility; the susceptibility slowly rises, but at the upper limit of the present measurements has reached a value which corresponds only to a magnetic moment of 4·97 B.M.

[3] F. A. COTTON, A. D. LIEHR and G. WILKINSON, *J. Inorg. Nucl. Chem.* **1**, 175 (1955).
[4] J. VOITLÄNDER and E. SCHMITSCHEK, *Z. Elektrochem.* **61**, 941 (1957).

When the liquid is cooled, the susceptibility curve retraces its path and, on supercooling, continues smoothly past the discontinuity at the melting point. Reliable data for the liquid–supercooled liquid curve could not be obtained below 0°C, for the supercooled liquid congealed and contracted into segments in the Gouy tube, leaving voids in the necessarily uniform packing. Analysis of these data shows that they do

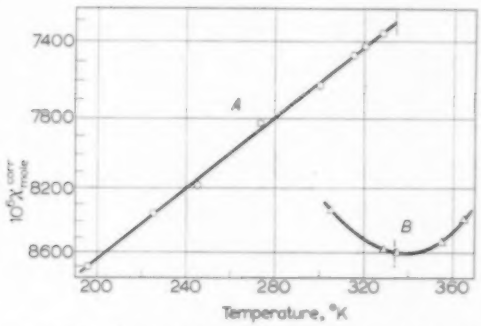

FIG. 1.—Magnetic susceptibility of manganese methyl*cyclo*pentadienide.
A ○, crystalline solid;
B △, liquid.

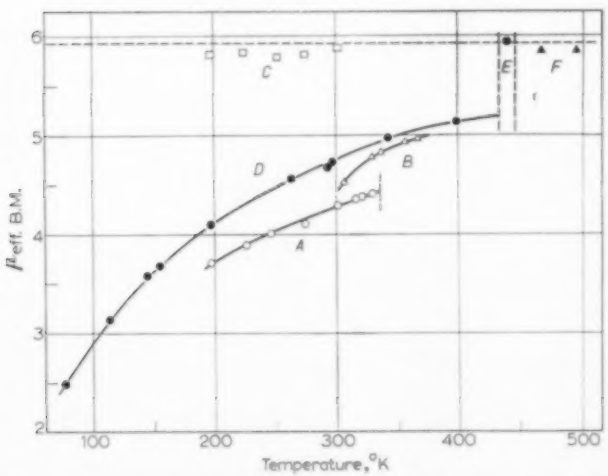

FIG. 2.—Magnetic susceptibilities of manganese *cyclo*- and methyl*cyclo*pentadienides.
Methyl*cyclo*pentadienide. *A*, ○, crystalline solid; *B*, △, liquid; *C*, □, solution in tetrahydrofuran.
*cyclo*Pentadienide. *D*, ●, crystalline solid, brown form; *E*, ●, crystalline solid, pink form; *F*, ▲, liquid.

not fit a Curie–Weiss law ($1/\chi \propto T + \theta$); indeed the slope of $1/\chi$ vs. T below the compound's melting point is negative and non-linear, yielding negative values of c and imaginary "effective moments".

In 0·415 M solution in tetrahydrofuran over the temperature range 195–300°K, manganese methyl*cyclo*pentadienide follows the simple Curie law, with $\mu_{eff} = 5{\cdot}83$ B.M.; we should expect $\mu_{eff} = 5{\cdot}92$ B.M. for five unpaired electrons (spin only).

The agreement of the moments for the magnetically dilute compounds with the

theoretical value indicates essentially ionic bonding of the rings to the metal atom. Likewise, the close similarity between the susceptibilities of the brown crystalline forms of the compounds suggests similar antiferromagnetic interaction. As for the peculiar behaviour of liquid manganese methyl*cyclo*pentadienide, it would appear that two effects are operative: a partial antiferromagnetic ordering superimposed on a temperature-dependent disordering of the liquid. There may be aggregation of molecules into clusters or micelles with sufficient orientation to permit partial magnetic ordering, yet without sufficient order to permit crystallization—a sort of mesomorphism or "liquid crystal" situation. To our knowledge this magnetic phenomenon has not previously been observed since most transition metal compounds which have been investigated in detail have been binary compounds with high melting points and highly symmetrical particles in the melt. If this interpretation is correct, at some higher temperature the magnetic moment of the liquid should attain an unordered, spin-only value of 5·29 B.M. either by continuous rise, or by a second discontinuous jump corresponding to complete breakdown of the liquid structure. Further, properties such as density, viscosity and specific heats of the liquid should show anomalous behaviour correlative with the magnetic properties.

Considerably more extensive and detailed study will be required before a clear understanding of the behaviour of manganese methyl*cyclo*pentadienide is reached.

EXPERIMENTAL

An analysis of the commercial methyl*cyclo*pentadiene dimer used (Enjay Company Inc., 15 West 51st Street, New York 19, N.Y.) gives methyl*cyclo*pentadiene (b.p. 72·3–72·6°), 94·3 per cent; *cyclo*pentadiene (b.p. 40·3–40·5°), 4·0 per cent; C_7 *cyclo*dienes, 1·0 per cent; butadiene, ~0·7 per cent; inhibitor, 550 p.p.m. If this dimer is merely cracked at atmospheric pressure and the monomer taken off through a 20 cm Vigreux column, pure methyl*cyclo*pentadiene is not obtained, since the depolymerization is not an equilibrium process and other diene components are released during depolymerization. The monomer was accordingly separately fractionated through a 40 cm Vigreux column with a reflux ratio ~2 : 1. The monomer was used at once. If this procedure is not used, impurities in the final metal–methyl *cyclo*pentadienyl derivatives, such as mixed *cyclo*pentadienyl–methyl*cyclo*pentadienyl derivatives are exceedingly difficult to separate from the methyl compounds even for stable compounds by chromatography. On a large scale, or in the case of air-sensitive compounds, purification is virtually impossible. Only by very careful purification of the monomer have we been able to obtain compounds with well defined melting points.

The compounds were, except where otherwise stated, prepared from sodium methyl*cyclo*pentadienide in tetrahydrofuran and the metal halide as with the *cyclo*pentadienyl compounds.[1] Methyl*cyclo*pentadiene reacts less rapidly with sodium than does *cyclo*pentadiene and the sodium sand tends to coagulate in large unreactive lumps; this was prevented by using a large volume of tetrahydrofuran (~1500 ml/mole sodium) and the solvent was refluxed whilst the diene was added slowly.

All preparations were carried out under nitrogen.

1:1′-*Dimethylferrocene*

Dimethyl ferrocene has been made by NESMEYANOV *et al.*[5] by lithium aluminium hydride reduction of the dicarboxylic acid; they give m.p. 29–30°. It has been made also in industrial laboratories from methyl*cyclo*pentadiene[6] and has been used in studies on substitution in ferrocene derivatives.[7]

The residue after removal of solvent (150 ml) from the reaction mixture of ferrous chloride (0·095 mole) and sodium methyl*cyclo*pentadienide (0·19 mole) was extracted with 100 ml petroleum ether. The latter was removed and the product fractionated at reduced pressure. Yield 12·8 g

[5] A. N. NESMEYANOV, E. G. PEREVALOVA and Z. A. BEINORAVIEHUTE, *Dokl. Akad. Nauk SSSR* **112,** 439 (1957).
[6] Cf. *Brit. Pat.*, (Dupont) 764058 (*Chem. Abstr.* **52,** 580 (1958).
[7] K. L. RINEHART, JR., K. L. MOTZ and S. MOON, *J. Amer. Chem. Soc.* **79,** 2749 (1957).

(63 per cent on $FeCl_3$), b.p. 115°/10 mm, m.p. 37–39°C. (Found: Fe, 26·1; C, 67·35; H, 6·39. Calc. for $C_{12}H_{14}Fe$: Fe, 26·09; C, 67·32; H, 6·59%). 1 : 1′-dimethylferrocene can be super-cooled, but crystallization is easily induced or begins spontaneously within an hour or so at 30°. The compound is much more readily oxidized than ferrocene. Solutions in ethanol are slowly oxidized by air and warm carbon tetrachloride or chloroform cause extensive decomposition.

The polarographic behaviour was determined with a Sargent Model 11 polarograph in a divided H-cell with saturated calomel reference electrode, chloride ion being excluded from the solution by a potassium nitrate–agar plug. In a 90% ethanol, 0·1 M sodium perchlorate and 0·01 M perchloric acid supporting electrolyte, 1 : 1′-dimethylferrocene shows a well defined reversible anodic wave at a half-wave potential +0·38 V vs SCE or −0·49 V vs NHE on Latimer's scale.

The blue cation $[C_{12}H_{14}Fe]^+$ gives the usual precipitates with large anions.

1:1′-Dimethylnickelocene

Addition of sodium methyl*cyclo*pentadienide (0·2 mole) in 250 ml tetrahydrofuran to anhydrous nickel bromide (0·1 mole) in 100 ml tetrahydrofuran gave a solution containing the product; essentially none was formed on using nickel chloride. The solvent was removed and the residue extracted with from 50 ml portions of petroleum ether; the dark green extract was allowed to stand and after ~12 hr was filtered. The solvent was stripped and the green oil distilled five times at about 1 mm at 85–90°. The centre fraction of the final distillation had m.p. 36–38°. (Found: Ni, 26·95; Calc. for $C_{12}H_{14}Ni$: Ni, 27·04%). Yield 7·9 g (36 per cent on $NiBr_2$). The compound forms dark green elongated prisms which are rapidly decomposed by air as are its solutions. It is instantly decomposed by chlorinated hydrocarbons and carbon disulphide. It is paramagnetic and follows the Curie law with $\mu_{eff} = 2{\cdot}9$ B.M.; including a diamagnetic correction of 115×10^{-6} cgs units, $\chi_{mol}^{307°K} = 3600 \times 10^{-6}$ cgs units, $\chi_{mol}^{196°K} = 5500 \times 10^{-6}$ cgs units, $\chi_{mol}^{82°K} = 12{,}400 \times 10^{-6}$ cgs units.

*Manganese methyl*cyclo*pentadienide*

To anhydrous $MnCl_2$ (0·175 mole) was added sodium methyl*cyclo*pentadienide (0·40 mole) in 300 ml tetrahydrofuran. The mixture was refluxed 4 hr. After removal of solvent, the dark brown viscous residue was distilled at 250° under 0·1 mm pressure. About 40 g of a reddish oil was collected. After three distillations at ~1 mm pressure and 85–90°, rejecting foreruns and hold-up residues, the reddish-brown oil began to crystallize spontaneously. Further purification from oily impurities was effected by sublimation. Yield 24·6 g (66 per cent on $MnCl_2$) as dark brown crystals, m.p. 61–63°. (Found: Mn, 25·92; Calc. for $C_{12}H_{14}Mn$: 25·77%).

The compound is exceedingly sensitive to moisture and air and will inflame if warm. Further, the crystals have a marked coefficient of expansion and adhere to glass; heating the crystallized solid in a sealed Gouy tube, and the warming of a blocked condenser tube and a heavy-walled 100 ml. distilling flask containing 23 ml of the compound as solid, have caused disruption.

The magnetic susceptibility of the pure compound and of a 0·415 M solution in tetrahydrofuran are given in Table 1. Measurements as before[1] were made at field strengths ranging from 4680 to 9020 G. No field strength dependence exceeding the reproducibility of the experiment was detected.

*Methyl*cyclo*pentadienylmanganese tricarbonyl*

This compound has been described as a new antiknock material (AK-33X) in various technical papers (reports from the Ethyl Corporation, Detroit). We have also prepared it by the method used for the *cyclo*pentadienyl analogue.[1b] Crude methyl manganese *cyclo*pentadienide (from 0·08 mole $MnCl_2$) prepared as above was heated in an autoclave with carbon monoxide at 1000 psi and 200°C. The product was fractionally distilled and collected as a pale yellow liquid, b.p. 112°/10 mm, m.p. 1·7–2·0°C. Yield 70 per cent based on $MnCl_2$. (Found: 3, 49·5; H, 3·3; Mn, 25·2. Calc. for $C_6H_7Mn(CO)_3$: C, 49·60; H, 3·23; Mn, 25·20%).

Bis(*methyl*cyclo*pentadienyl*) *titanium dichloride*

Titanium tetrachloride (0·2 mole) in benzene (20 ml) was added dropwise to sodium methyl*cyclo*pentadienide in 300 ml tetrahydrofuran. The violent reaction produced much black solid which dissolved on refluxing for 4 hr. The red gel-like residue after removal of solvent was extracted with chloroform. Alternate crystallizations of the crude product (35 g) from toluene and chloroform

gave 14·2 g, yield 26 per cent on $TiCl_4$, m.p. 217–218° (with decomposition). (Found: Ti, 17·5; Cl, 25·6; C, 52·98; H, 5·38. Calc. for $C_{12}H_{14}TiCl_2$: Ti, 17·29; Cl, 25·60; C, 52·01; H, 5·09%). The compound is slightly soluble in polar organic solvents and moderately soluble in hot aromatic and polar solvents. It crystallizes in brilliant red, diamond-shaped leaflets which show excellent centred positive acute bisectrix figures and symmetrical extinction.

Bis(*methyl*cyclo*pentadienyl*) *zirconium dichloride*

This was prepared as the titanium compound. Evaporation of the chloroform extract gave a black tar; combination of 6 N hydrochloric acid and petroleum ether with this tar formed an emulsion from which a white solid could be centrifuged. This was crystallized from hot toluene saturated with hydrogen chloride and then from chloroform and butanone. Yield 38 per cent on $ZrCl_4$, m.p. 180–181° with slight decomposition. (Found: Zr, 29·8; Cl, 22·3; Calc. for $C_{12}H_{14}ZrCl_2$: Zr, 28·48; Cl, 22·14%).

The compound crystallizes in white diamond-shaped leaflets, closely resembling the titanium analogue in optical and solubility properties. It shows a pale blue fluorescence under ultra-violet light.

*Di-(methyl*cyclo*pentadienyl-tricarbonyl-molybdenum)*

Molybdenum carbonyl (0·05 mole) was refluxed in tetrahydrofuran (200 ml) with sodium methyl*cyclo*pentadienide (0·06 mole). The solution was evaporated and the solid suspended in 50 ml tetrahydrofuran and 6 ml glacial acetic acid in 50 ml solvent was added slowly. The solvent was removed and impure methyl*cyclo*pentadienyl tricarbonyl hydride separated by vacuum distillation as a pale yellow oil. Air oxidation of ether solutions of this compound gave the product which was crystallized from dichloromethane–petroleum ether by cooling. Yield 5·5 g (42 per cent on $Mo(CO)_6$), m.p. 146–147° decomposes. (Found: Mo, 37·02; Calc. for $C_{15}H_{14}Mo_2O_6$: Mo, 37·11%).

*Di-(methyl*cyclo*pentadienyl-dicarbonyl iron)*

Iron pentacarbonyl (0·10 mole) and purified (polymerisation of pure monomer) di-(methyl*cyclo*pentadiene) (0·075 mole) were heated at 170° in a 150 ml autoclave for 72 hr. Crystallization of the product from ether by cooling to −70° gave deep red leaflets, m.p. 98–99°. Yield 5·5 g (29 per cent on $Fe(CO)_5$). (Found: Fe, 29·02. Calc. for $C_{16}H_{14}Fe_2O_4$: 29·24%). The compound is quite soluble in organic solvents and the solutions decompose extensively within a day.

*Thallium methyl*cyclo*pentadienide*

To thallous sulphate (5·04 g) in 40% potassium hydroxide (10 ml) was added methyl*cyclo*pentadiene (3 ml); after stirring for 30 min the product was centrifuged and sublimed repeatedly at 75°C in vacuum. Yield 4·3 g (76 per cent on Tl_2SO_4). (Found: Tl, 71·7; Calc. for C_6H_7Tl: Tl, 72·09%).

The compound forms pale yellow needles, m.p. 88–89° with slight decomposition. It is vigorously oxidized by air.

*Neodymium methyl*cyclo*pentadienide*

Neodymium chloride (0·01 mole) was added to sodium methyl*cyclo*pentadienide (0·05 mole) in tetrahydrofuran, and after stirring for 2 hr the solvent was removed and the product sublimed directly from the residue in vacuum at 200°C. Yield ~70 per cent based on $NdCl_3$. (Found: Nd, 37·7; Calc. for $C_{18}H_{21}Nd$: Nd 37·8%).

The compound forms reddish-blue crystals, m.p. 165°; it is rapidly decomposed by air and water.

Infra-red measurements

Measurements were made using a Perkin–Elmer Model 21 instrument.

$[CH_3C_5H_4Fe(CO)_2]_2$ in CS_2 and CCl_4: 3080*w*, 2950, 2900, 2850*w*, 2050*m*, 1999*vs*, 1953*vs*, 1923*sh,m*, 1791*sh,m*, 1779*vs*, 1486, 1453*m*, 1389*w*, 1375*m*, 1350*vw*, 1060*w*, 1044*m*, 1033*m*, 928*m*, 844*sh,s*, 836*s*, 828*s*, 645*vs*.

$[CH_3C_5H_4Mo(CO)_3]_2$ in CS_2 and CCl_4: 3090*w*, 2960, 2920, 2820*vw*, 2057*w*, 2016*w*, 1984*m*, 1955*vs*, 1914*vs*, 1515*m*, 1480, 1460*m*, 1390, 1375*w*, 1062*w*, 1044*w*, 1034*m*, 941*vw*, 922*vw*, 870*m*, 816*s*.

$CH_3C_5H_4Mn(CO)_3$ in CS_2 and CCl_4: 3090*w*, 2960*w*, 2940*w*, 2900*sh*, 2870*sh*, 2033*vs*, 1940*vs* 1485*m*, 1460*m*, 1380*m*, 1355*w*, 1240*w*, 1210*w*, 1155*w*, 1130*w*, 1065*m*, 1045*s*. 1035*s*, 980*w*, 955*m*, 840*s*, 750*s*, 670*s*.

$C_{12}H_{14}TiCl_2$ in KBr: 3110*m*, 2920*m*, 2860*w*, 1740*vw*, 1645*vw*, 1510*s*, 1462*m*, 1425*w*, 1375*s*, 1260*vw*, 1247*vw*, 1083*vw*, 1055*s*, 1040*w*, 1033*w*, 939*w*, 871*m*, 859*vs*, 829*m*, 701*m*.

$C_{12}H_{14}ZrCl_2$ in KBr: 3110*w*, 2920*m*, 2860*w*, 1500*m*, 1458*m*, 1416*vw*, 1375*m*, 1244*m*, 1078*vw*, 1052*s*,*sh*, 1046*s*, 1038*s*, 938*w*, 881*vw*, 856*s*, 843*vs*, 817.

$C_{12}H_{14}Fe$ in CS_2 and CCl_4: 3090*m*, 2960*m*, 2920*m*, 2880*m*, 1750*w*, 1730*w*, 1680*w*, 1640*w*, 1515*m*, 1480*m*, 1455*m*, 1380*w*, 1370*w*, 1155*m*, 1038*s*, 1024*s*, 920*m*, 850*w*, 823*s*, 804*s*.

Acknowledgements—We are indebted to the National Science Foundation for a predoctoral fellowship to one of us (L. T. R.) and to the Mallinckrodt Fund for assistance with research expenses.

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LETTERS TO THE EDITORS

On the first equilibrium steps in the acidification of the molybdate ion

(*Received* 6 *August* 1958)

IT is generally agreed that the molybdate ion in alkaline solution exists in the form of MoO_4^{2-}, and that on acidification, polynuclear complexes are formed. However, there is considerable confusion regarding the formulae of the latter. For instance, JANDER *et al.*[1] claim the existence of $Mo_2O_{11}^{6-}$, $HMo_2O_{11}^{3-}$, $HMo_6O_{21}^{5-}$, $H_2Mo_6O_{21}^{4-}$, $H_3Mo_6O_{21}^{3-}$, $H_7Mo_{12}O_{41}^{3-}$, $H_7Mo_{24}O_{78}^{5-}$, and $H_9Mo_{24}O_{78}^{3-}$. BYÉ[2] claims the existence of $Mo_7O_{24}^{6-}$, $Mo_6O_{20}^{6-}$, $Mo_4O_{13}^{2-}$, and $HMo_6O_{20}^{3-}$. A survey of work up to 1950 was made in the dissertation of LINDQVIST.[3]

By X-ray crystallographic measurements, LINDQVIST could confirm the existence of the ions $Mo_7O_{24}^{6-}$ and $Mo_6O_{20}^{4-}$ in crystal structures;[3,4] from spectrophotometric measurements he also found evidence for these ions in solution.[5]

Some time ago, Y. SASAKI started a study of molybdate equilibria, applying the experimental technique and the graphical and mathematical methods developed by SILLÉN *et al.*[6] in Stockholm. All equilibria were studied at 25°C, with $NaClO_4$ as ionic medium, the sodium ion concentration, $[Na^+]$, being kept constant at 3 M.

The cells used were of the type

RE/solution/glass electrode, or RE/solution, Q,QH_2/Pt, where

RE = Ag,AgCl/0·01 M $AgClO_4$, 2·99 M $NaClO_4$/3 M $NaClO_4$.

By calibrating with solutions of known H^+ concentration and the same ionic medium, it was possible from the measured e.m.f. to calculate $(H^+) = h$ in each solution. From the analytical data one knows B (the total molybdate concentration), and H (the excess of protons over MoO_4^{2-} and H_2O) From the data one may calculate the average number of H^+ that have been taken up per MoO_4^{2-}, $Z = (H - h)B^{-1}$, and the average charge per Mo, $z = Z - 2$.

In Fig. 1, Z and z are plotted as functions of log h, up to $Z = 1{\cdot}4$ ($z = -0{\cdot}6$). Each series of points corresponds to experiments having the same value of B; nine values of B, between 0·6 mM and 160 mM, were used. The curves are calculated with the reactions and equilibrium constants given below.

By straightforward mathematical analysis of the data, using methods previously worked out in this laboratory,[6] it was deduced that the main complex formed is $Mo_7O_{24}^{6-}$. Strictly speaking, the equilibrium data can only give the number of molybdenum atoms in the complex (which is seven), and the charge (6−), but cannot distinguish between complexes with various water contents. Thus the assignment as $Mo_7O_{24}^{6-}$, and not for instance $(MoO_3)_7(OH)_6^{6-}$, is based on the evidence from crystal structures.[3,4]

Deviations at low concentrations and low values of Z could be explained assuming $HMoO_4^-$ to be the only mononuclear complex besides MoO_4^{2-}; with only H_2MoO_4 the agreement would not be so good. However, our data are not incompatible with those of SCHWARZENBACH and MEIER,[7] who found H_2MoO_4 to be the predominating species at higher Z.

[1] G. JANDER, K. F. JAHR and W. HEUKESHOVEN, *Z. Anorg. Chem.* **194**, 383 (1930).
[2] J. BYÉ, *Ann. Chim.* (France), **20**, 463 (1945). (diss, Paris); *C.R. Acad. Sci., Paris* **238**, 239 (1954); *Bull. Soc. Chim. Fr.* 1023 (1957).
[3] I. LINDQVIST, *Nova Acta Regiae Soc. Sci. Upsaliensis* ser IV, **15**, Nr 1 (1950).
[4] I. LINDQVIST, *Arkiv Kemi* **2**, 325 (1950); *Acta Cryst* **3**, 159 (1950).
[5] I. LINDQVIST, *Acta Chem. Scand.* **5**, 568 (1951).
[6] S. HIETANEN and L. G. SILLÉN, *Acta Chem. Scand.* **6**, 747 (1952); G. BIEDERMANN and L. G. SILLÉN, *Arkiv Kemi* **5**, 425 (1953); L. G. SILLÉN, *Acta Chem. Scand.* **8**, 318 (1954); **10**, 186, 803 (1956); F. ROSSOTTI and H. ROSSOTTI, *Acta Chem. Scand.* **10**, 957 (1956).
[7] G. SCHWARZENBACH and J. MEIER, *J. Inorg. Nucl. Chem.* **8**, 302 (1958).

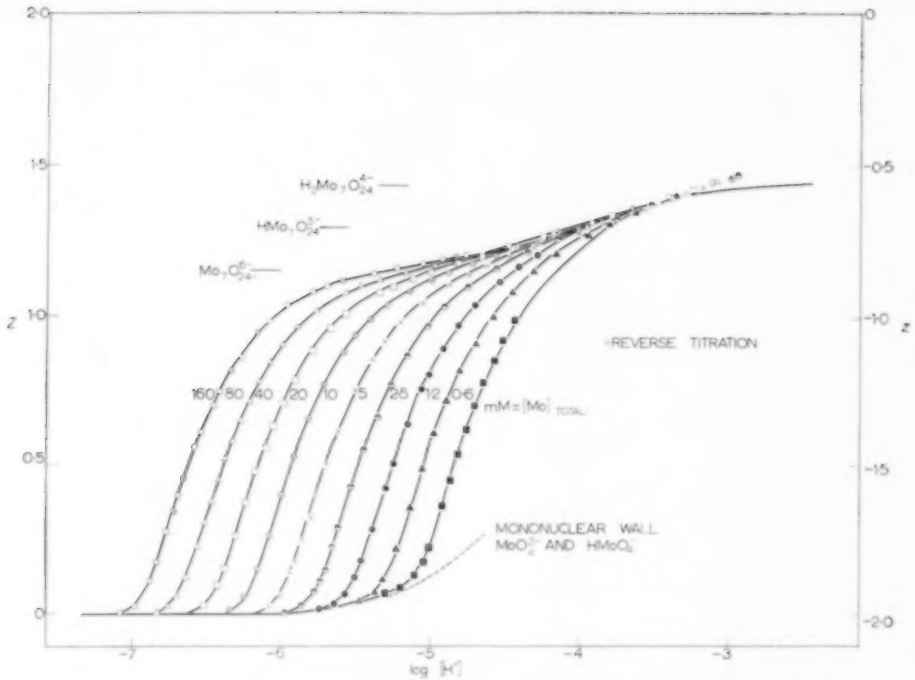

FIG. 1.—Equilibria on acidification of molybdate ion (3 M $NaClO_4$, 25°C). Horizontal axis: log h. Vertical axis: z (average charge per Mo atom) and Z (average number of protons bound per MoO_4^{2-}). Points: experimental points for various total concentrations of Mo. For the highest Mo concentration, different symbols refer to titrations in opposite directions. Full curves, calculated with the reactions and equilibrium constants given in the text.

Between $z = -1{\cdot}2$ and $-0{\cdot}6$, it was deduced from the data that the species $HMo_7O_{24}^{5-}$ and probably also $H_2Mo_7O_{24}^{4-}$, are formed.

The following equilibrium constants were deduced:

Reaction	log K
$MoO_4^{2-} + H^+ \rightleftharpoons HMoO_4^-$	$4{\cdot}08 \pm 0.15$
$7\,MoO_4^{2-} + 8\,H^+ \rightleftharpoons Mo_7O_{24}^{6-} + 4\,H_2O$	$57{\cdot}7 \pm 0{\cdot}2$
$Mo_7O_{24}^{6-} + H^+ \rightleftharpoons HMo_7O_{24}^{5-}$	$4{\cdot}33 \pm 0{\cdot}02$
$HMo_7O_{24}^{5-} + H^+ \rightleftharpoons H_2Mo_7O_{24}^{4-}$	$\approx 3{\cdot}7$

The last species is somewhat uncertain; at one end of the region where it would be important, there are deviations indicating other complexes as well. The equilibria at $z > -0{\cdot}6$ are now being investigated by Y. SASAKI.

The agreement obtained over a wide range of concentrations and pH seems to be quite satisfactory. We think it is unlikely that as good agreement could be obtained substituting any other mechanism for the three first reactions.

Full details of the work will be published elsewhere. It has been supported by the Swedish Natural Science Research Council.

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High resolution nuclear-magnetic-resonance spectra of the N-methyl silylamines

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CURRENT interest in the chemistry of the silylamines has led us to obtain the hydrogen (proton) nuclear-magnetic-resonance spectra of trisilylamine, N-methyl-disilylamine, N-dimethyl-silylamine and trimethylamine. The experimental results are collected in Table 1; all the main resonances listed occurred as sharp bands without resolvable structure. Additional weak and widely spaced satellites (also without structure) were caused by ^{29}SiH and ^{13}CH groups.

TABLE 1.—HYDROGEN NUCLEAR-MAGNETIC-RESONANCE DATA FOR TRISILYLAMINE, THE N-METHYL SILYLAMINES, AND TRIMETHYLAMINE

Compound	CH_3 resonance*	SiH_3 resonance*	$J\uparrow_{^{13}CH}$	$J\uparrow_{^{29}SiH}$
$N(CH_3)_3$	$3{\cdot}2_0$	—	132	—
$SiH_3N(CH_3)_2$	$3{\cdot}0_0$	$1{\cdot}0_0$	134	208
$(SiH_3)_2NCH_3$	$2{\cdot}6_7$	$0{\cdot}9_0$		212
$(SiH_3)_3N$	—	$0{\cdot}9_0$	—	212

* Measured in chemical shift (δ) units of parts per million in 5 per cent solution in *cyclo*hexane, the *cyclo*hexane resonance being assumed to have $\delta = +3{\cdot}9$ relative to water.
† Measured in c/s with pure liquid samples.

The chemical shift values of the CH_3 resonances change appreciably for the series of molecules, whereas the SiH_3 resonance remains virtually constant. The change in the methyl resonance is to lower fields from trimethylamine to the monomethyl-disilyl compound, and implies that the protons bound to carbon become less shielded as the methyl groups are replaced by silyls, i.e., that such replacement makes the nitrogen atom effectively more electronegative.

It is interesting to note that this is in keeping with other properties of the silylamines. Towards simple acceptors, the order of basicity of the molecules is $N(CH_3)_3 > (SiH_3)N(CH_3)_2 > (SiH_3)_2NCH_3 \simeq (SiH_3)_3N$;[1,2] the same is true of the analogous series of amines containing the CH_3SiH_2-radical.[3] This electron-withdrawing behaviour of silyl groups is believed to be due to $(p$–$d)\pi$-bonding from nitrogen to silicon;[1,3] the same ideas account for the planar arrangement of the heavy atoms in trisilylamine.[4,5]

As might be expected, the change in chemical shift of the SiH_3 groups is in the same direction as for the CH_3 groups; it is, however, much smaller in magnitude, showing that the lone pair of electrons on the nitrogen atom has a much less pronounced effect on the shielding of the protons of the silyl group.

The chemical shifts were also measured in samples of the pure liquids to which a drop of *cyclo*hexane had been added as an internal standard. A change in chemical shift, larger than the experimental error, was observed only in the case of the methyl resonance of N-dimethyl-silylamine; the δ-value here was $2{\cdot}8_5$ as compared with $3{\cdot}0_0$ in dilute solution. This appreciable change of the CH resonance on dilution implies the presence of stronger intermolecular forces than for the other molecules, and may be correlated with the much higher melting point of this compound ($+3°$)[1] as

[1] S. SUJISHI and S. WITZ, *J. Amer. Chem. Soc.* **76**, 4631 (1954).
[2] A. B. BURG and E. S. KULJIAN, *J. Amer. Chem. Soc.* **72**, 3103 (1950).
[3] E. A. V. EBSWORTH and H. J. EMELÉUS, *J. Chem. Soc.* 2150 (1958).
[4] K. HEDBERG, *J. Amer. Chem. Soc.* **77**, 6491 (1955).
[5] E. A. V. EBSWORTH, J. R. HALL, M. J. MACKILLOP, D. C. MCKEAN, N. SHEPPARD and L. A. WOODWARD, *Spectrochim. Acta* **13**, 202 (1958).

compared with those of trisilylamine (−106°),[6] N-methyl-disilylamine (−124°),[1] and trimethylamine (−117°).[7] Once again, the change is not reflected by any corresponding change in the resonance of the protons bound to silicon.

Although they do not exhibit significant trends, we also list for completeness in the table the spin-spin coupling constants (J) of H with ^{29}Si and ^{13}C.

EXPERIMENTAL

Trisilylamine and N-methyl-disilylamine were prepared by mixing excess of silyl chloride vapour with either ammonia[2,6] or methylamine[8] in the vapour phase. N-Dimethyl-silylamine was made similarly from dimethylamine and silyl iodide. Each compound was purified by low temperature fractional distillation, and its purity was tested by measurements of vapour-pressure and vapour-density.

Measurements were made on the pure liquids (to each sample of which one drop of cyclohexane was added as an internal standard), and on approximately 5 per cent solutions in the same solvent. The spectra were obtained with a Varian Associates V-4300B high-resolution nuclear-magnetic-resonance spectrometer with flux stabilizer, using the sample spinning technique. The samples were contained in Pyrex tubing of 5 mm outside diameter. Frequencies were measured relative to *cyclo*hexane as internal standard and are accurate to ±2 c/s (±0·05 in δ units).

We are grateful to the Hydrocarbon Research Group of the Institute of Petroleum for a grant, and to the Wellcome Foundation, who have lent the spectrometer to the Department. We would like to thank Dr. A. G. Maddock for helpful discussions.

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[6] A. Stock and C. Somieski, *Ber. Dtsch. Chem. Ges.* **54**, 740 (1921).
[7] J. G. Aston, M. L. Sagenkahn, G. J. Szasz, G. W. Moessen and H. F. Zuhr, *J. Amer. Chem. Soc.* **66**, 1171 (1944).
[8] H. J. Emeléus and N. Miller, *J. Chem. Soc.* 817 (1939).

The half-life of ^{89}Sr

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Herrman and Strassman published an article early in 1955[1] giving the half-life of ^{89}Sr as 50·5 ± 0·2 days. This result was obtained by measuring the decay of ^{89}Sr obtained by slow neutron fission of uranium. It was confirmed by similar measurements on ^{89}Sr produced by neutron irradiation both of natural strontium and also of strontium enriched to 99·3% ^{88}Sr, and thirdly, by the (n, p) reaction on yttrium. In the following year Kjelberg and Pappas[2] reported a value of 51 ± 1 day for the half-life of ^{89}Sr which they obtained by the fission of uranium with 170 MeV protons and the value quoted in *Nuclear Science Abstracts* has been 50 or 51 days as from the 1955 cumulation. Despite this, there still appear articles in which reference is made to ^{89}Sr having a half-life of up to 54 days, this presumably being a legacy of earlier years when several values ranging from 53 to 55 days were quoted.[2–7]

[1] G. Herrmann and F. Strassmann, *Z. Naturf.* **10** A, (2), 146 (1955).
[2] A. Kjelberg and A. Pappas, *Nucl. Phys.* **1**, 322 (1956).
[3] D. Stewart, J. Lawson and J. Cork, *Phys. Rev.* **52**, 901 (1937).
[4] C. Lieber, *Naturwissenschaften* **27**, 421 (1939).
[5] W. Grummitt and G. Wilkinson, *Nature, Lond.* **158**, 163 (1946).
[6] R. Goeckermann and I. Perlman, *Phys. Rev.* **76**, 628 (1949).
[7] C. D. Coryell and N. Sugarman, *Radio Chemical Studies; The Fission Products*, NNES, Vol. II, Paper 76. McGraw Hill, New York (1951).

The work carried out in our laboratories on the world-wide deposition of fission products from nuclear explosions entails calibration of β-counters with sources prepared from standardized solutions of certain pure radio-nuclides including ^{89}Sr. Towards the end of 1956 10 mg of strontium, enriched in ^{88}Sr to 99·3 per cent, were obtained in the form of oxalate and irradiated in BEPO, Harwell, for four weeks. The oxalate was then dissolved in dilute nitric acid and the ^{89}Sr solution calibrated by 4π counting. Strontium carbonate sources were prepared for counter calibration by adding suitable aliquots of this solution to various amounts of inactive strontium carrier followed by precipitation with ammonium carbonate. The decay of the activity of one of these sources containing 15 mg strontium was followed from March 1957 to February 1958 and the values obtained are given in Table 1. The efficiency and background of the EHM 2 thin-window tube used for the measurements were checked regularly over the whole period.

TABLE 1.—^{89}Sr DECAY DATA

Total count	Counts/min (including background and paralysis corrections)	Decay time (hr)
100,000	946	0
98,000	817	312
172,000	639	744
139,000	544	1008
78,000	478	1251
60,000	391	1587
105,000	339	1850
49,000	285	2091
73,000	247	2330
11,000	213	2591
28,000	191	2835
25,000	152	3240
131,000	116	3684
100,000	93·8	4069
130,000	79·7	4361
29,000	65·8	4681
8300	54·1	4996
15,000	39·6	5618
40,000	29·1	6109
18,500	11·0	7740

The half-life of the ^{89}Sr was calculated to be 50·36 days and this was verified by the Computing Group, Theoretical Physics Division, A.E.R.E., who reported a value of 50·360 days with a standard error of 0·163 days. The total error may be more than this due to the presence of contaminating radio-nuclides of which only ^{85}Sr and ^{90}Sr would be expected to introduce any measurable effect. ^{85}Sr ($t_{\frac{1}{2}} = 65$ days) is formed by an (n, γ) reaction on any ^{84}Sr remaining in the Sr which had been enriched in ^{88}Sr, and ^{90}Sr is produced by the ^{89}Sr itself undergoing an (n, γ) reaction. It has been calculated from data including the thermal neutron cross-sections for ^{84}Sr and for ^{89}Sr,[8] the thermal neutron flux in the pile and the time of irradiation that the possible error arising from these isotopes could not have exceeded $+0·05$ days.

The following experiments were carried out to confirm this figure and to see whether in fact the error arising from these contaminants might be even less, since where there were uncertainties in the data, values were taken which would lead to a maximum effect on the half-life:

(a) An aliquot of the active solution from which the Sr source was prepared was examined by γ-spectrometry for ^{85}Sr. No 0·51 MeV γ-activity was detected but HUNTER[9] fixed an upper limit for this activity and it was then calculated that the effect on the recorded half-life would be $< 0·01$ days.

[8] L. ROY and J. ROY, *Canad. J. Phys.* **35**, 1215 (1957).
[9] G. HUNTER, Woolwich Outstation, A.E.R.E. Personal communication, June 1958.

(b) A second aliquot of the ^{89}Sr solution was taken for ^{90}Sr estimation. This was done by adding Sr and Y carriers, storing for 18 days, separating the ^{90}Y which would have grown into radioactive-equilibrium with any ^{90}Sr present and counting the resulting Y source at suitable intervals in a low background counter. A value for ^{90}Sr was found that would introduce an error of $< 0{\cdot}01$ days in the ^{89}Sr half-life calculated.

Taking into account the possible contributions from ^{85}Sr and ^{90}Sr we conclude that the half-life of ^{89}Sr is $50{\cdot}36 \pm 0{\cdot}18$ days. This is in good agreement with the value reported by KJELBERG and PAPPAS and the average value of HERRMANN and STRASSMANN, although the latters' result using ^{89}Sr formed by irradiation of strontium enriched in ^{88}Sr was somewhat lower ($49{\cdot}4 \pm 0{\cdot}1$ days). Results published in earlier years were rather higher than any of these but comment is often not possible due to the absence of certain information in the articles. However, in the case of perhaps one of the most important earlier papers[7] where the ^{89}Sr was produced by plutonium fission, only a relatively small increase in the counting rate subtracted for the long-lived ^{90}Sr contribution would alter the ^{89}Sr half-life very considerably.

Acknowledgements—We wish to acknowledge the Isotope Division A.E.R.E. for providing the enriched material and for carrying out the irradiation and subsequent calibration: also the Computing Group of the Theoretical Physics Division for their statistical appraisal of our results. Thanks are due to the Director, A.E.R.E. for permission to publish this letter.

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Exchange processes in halogen fluorides

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THE nuclear magnetic resonance spectra of various halogen fluorides have been discussed by MUETTERTIES and PHILLIPS,[1] who confirmed that chlorine trifluoride has a structure of C_{2v} symmetry; fluorine exchange between molecules was ascribed to dimer formation with an activation energy of 4·8 kcal.

The present investigation originated in an attempt to develop analytical methods for this class of compound, and involved an examination of the spectra of various binary mixtures, from which two results emerged. First, that the fluorine atoms in bromine pentafluoride molecules are incapable of exchanging rapidly with those of other fluorides such as HF, ClF_3, ClF, BrF_3, since its spectrum is unaffected by the presence of these compounds. Second, that these four other halogen compounds are capable of rapid mutual fluorine interchange, because mixtures give rise to collapsed spectra at frequencies which are roughly dependent on the relative amounts of the constituents.

Two experiments were made to test whether the presence of hydrogen fluoride is responsible for the collapsed spectra exhibited by impure samples of chlorine trifluoride—a phenomenon noted previously,[1] and necessitating an elaborate procedure for purification by distillation. In the first of these, a sample of commercial chlorine trifluoride was twice distilled and shown to give rise to a broad fluorine resonance at $-60°C$. The electromagnet was then recycled for the proton signal, when a small response was obtained under conditions of high sensitivity. In a second experiment,

[1] E. L. MUETTERTIES and W. D. PHILLIPS, *J. Amer. Chem. Soc.* **79**, 322 (1957).

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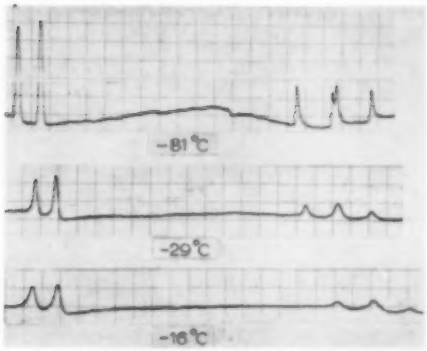

FIG. 1.—Effect of temperature on the ^{19}F spectrum of purified CLF_3. (H_0 = 10 kg).

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a sample of chlorine trifluoride was allowed to stand for 12 hr over dry sodium fluoride, both in the sample vessel and when condensed in the probe, in order to remove any traces of HF which might be present. The spectrum of the purified material then consisted of a very sharp doublet and triplet. This time, however, no proton signal could be found. It is thus possible to corrrelate the presence of trace quantities of hydrogen fluoride with the display of broad line spectra.

The temperature-dependence of the spectrum of "pure" chlorine trifluoride is shown in Fig. 1 and differs somewhat from the results of MEUTTERTIES and PHILLIPS, who observed that spin–spin coupling had disappeared at −15°C. Although the behaviour of each of several samples was

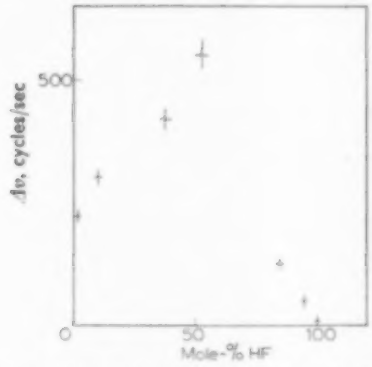

FIG. 2.—Effect of composition on the half-peak width of the ^{19}F resonance for the system ClF_3–HF (−30°C).

reproduceable throughout a temperature cycle, the precise temperature at which spin–spin coupling disappears varied from sample to sample; this suggested that traces of impurities (presumably HF) were still present. In one case spin–spin coupling was still very pronounced at 0°C. Moreover, recent evidence for the existence of azeotopes in the system ClF_3–HF[2,3] casts some doubt on the purification methods used in the earlier work.[1] It is thus not yet proven that exchange will occur between ClF_3 molecules in the complete absence of hydrogen fluoride, but if it does take place these results show that the activation energy must be significantly greater than 4·8 kcal. Moreover, the dramatic effect of adding trace quantities of HF suggests that in these compounds ionization is a more important mechanism than association.

Lastly, conditions were varied to test the effect of various parameters on the shape of the collapsed line displayed by the system HF–ClF_3. The greatest change in width resulted from alterations in the composition of the binary mixture, and Fig. 2 shows the variation in half-peak width plotted as a function of the concentration of HF monomer at −30°C. There is a pronounced maximum roughly corresponding to an equi-molar mixture of HF and ClF_3, which has not yet been explained. Although a molecular complex HF–ClF_3 was reported to exist in the vapour phase,[4] it has not been observed in liquid mixtures.[2]

The investigation is being continued in an attempt to understand the behaviour of these interesting compounds more fully.

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A method of adjusting pH without introducing extraneous captions or anions*

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FREQUENTLY in preparing very pure solutions prior to physical measurements, it is desirable to adjust the pH of such solutions to a predetermined value. In recent work being performed at the Ames Laboratory of the A.E.C. on conductivities and transference numbers of scandium salt solutions, it was necessary to titrate such solutions to the equivalence point with subsequent adjustment of the entire sample to this point prior to measurement.

The solution desired is one that would result if a pure sample of the anhydrous salt were placed in water and allowed to come to equilibrium:

$$Sc^{3+} + H_2O \rightleftharpoons Sc(OH)^{2+} + H^+$$

Since for this equilibrium the concentrations of H^+ and $Sc(OH)^{2+}$ type ions would be equal (neglecting the ion product of water for moderate concentrations of Sc^{3+}), the pH of such a solution could be designated as the equivalence point. To find such a point, titration with a 0·1 N solution of the anion acid is necessary.

To obtain a good titration curve, the pH of the original solution needs to be above the equivalence point before starting the titration. In trying to prepare solutions much above the equivalence point by adding an excess of Sc_2O_3 and filtering it off, the pH which resulted was not high enough to give a good titration curve. If one could add OH^- ions without introducing an accompanying cation, it would be highly desirable. Anion exchange resins are ideally suited to do just this because the cation is in the form of insoluble, filterable, beads.

The general procedure is as follows:

(1) Prepare OH^- form anion resin by passing carbonate-free NaOH or KOH[1] over the bed until no Cl^- can be detected in the effluent stream by acidifying with HNO_3 and treatment with $AgNO_3$. (Amberlite IRA-400 or Dowex-1, 50–100 mesh, Cl^- form resins are suitable for this purpose.)

(2) Add a sufficient amount of this hydroxide-form resin, with stirring, to the solution to raise the pH considerably above the suspected equivalence point. A good mechanical stirrer should be used during this stage to prevent scandium hydroxide particles from clinging to the resin beads.

(3) Filter off the insoluble resin beads.

(4) Titrate the solution to the equivalence point with the anion acid.

(5) Boil the solution for 1–2 hr. (This cannot be done with $Sc(NO_3)_3$ because boiling forms insoluble $Sc(OH)(NO_3)_2$. In this case, heating below boiling with a heat lamp for two days was sufficient.) This helps to break up any undissolved colloidal particles.

(6) Repeat steps 4, 5 until the pH stays constant.

Since the order of increasing affinity for the resin is: $OH^- < Cl^- < Br^- < NO_3^- < I^- < ClO_4^-$, the method outlined above should give satisfactory results with any of the above anions because the reactions:

$$\overline{R}OH + A^- \rightleftharpoons \overline{R}A + OH^-$$

$$C^{+n} + OH^- \rightleftharpoons COH^{+(n-1)}$$

have equilibria favouring the right sides where $\overline{R}$ is the insoluble resin cation, C is the salt cation, and A is the anion of the desired salt. Titration with the acid corresponding to the anion of the salt then gives:

$$COH^{+(n-1)} + (n-1)A^- + HA \rightleftharpoons C^{+n} + nA^- + H_2O$$

This general procedure should work very well with any salt which hydrolyses at its equivalence point as long as the anion resin has a stronger affinity for the salt's accompanying anion than it does for the hydroxide ion.

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* Work was performed in the Ames Laboratory of the U.S. Atomic Energy Commission.

[1] J. E. POWELL and M. A. HILLER, *J. Chem. Educ.* **34**, 330 (1957).

J. Inorg. Nucl. Chem., 1959, Vol. 9, pp. 101 to 102. Pergamon Press Ltd. Printed in Northern Ireland

BOOK REVIEWS

M. BENEDICT and T. H. PIGFORD: **Nuclear Chemical Engineering.** McGraw-Hill, New York, 1957. 594 pp.

BY this work Professors BENEDICT and PIGFORD have announced the birth of a new science, namely Nuclear Chemical Engineering. This is the achievements of the chemical engineer in the field of nuclear energy.

Prof. BENEDICT is one of the two editors of the monograph *Engineering Development in the Gaseous Diffusion Process*. The authors are from the Massachusetts Institute of Technology and have contributed much to the atomic energy programme in their country.

The chapters dealing with the solvent extraction of uranium and plutonium as well as the chapters on isotope separation, six in all, constitute exactly half of the book. Worthy of mention is that the chapters on solvent extraction are certainly the best place for treating together all the different processes of nuclear reactor materials. This book was much wanted by chemical engineers who are working in the field of atomic energy. A very good feature of the book is that it includes the material discussed at the Geneva Conference of 1955 for the Peaceful Uses of Atomic Energy. The book includes also a very valuable Appendix in 40 pages, "Properties of Nuclides" which gives the nuclear properties of isotopes as for example natural abundance, absorption cross-section for thermal neutrons, half-life and type of decay. The book is very well illustrated, full of tables, diagrams and flow sheets with full references to the original literature. Problems are to be found at the end of each chapter which are of great value to students.

This book, being one of the McGraw-Hill Series on Nuclear Engineering, is complementary to other books on this subject as for example that of Prof. STEPHENSON, who was lecturing last year in Vienna. What little overlapping there is to be found between the two books is definitely unavoidable.

In their book, BENEDICT and PIGFORD have put little emphasis on nuclear physics, as is to be expected, but they have strongly stressed the production of uranium, thorium and plutonium as well as other reactor materials. However, the production of reactor grade graphite is not treated at all. Some other topics of great interest to the chemical engineer are also not treated. There is for example no mention of heat transfer and corrosion (especially lacking for the liquid metals), ion exchange as applied to the recovery of trace amounts of uranium nor irradiation and the effect of highly active radiations on chemical reactions. Of course it is impossible to cover all the fields of nuclear chemical engineering in one book of this size and we hope that supplementary volumes will be published later to complete the subject.

In this book there is also material published for the first time. For example the thermodynamics of extraction of uranium by tributyl phosphate. Also their treatment of the term neutron cross-section is easily understood by chemists because they considered it from the point of view of chemical kinetics.

The book is highly recommended for every chemical engineer who wants to study this new branch of chemical engineering.

F. HABASHI

Proceedings of the International Symposium on Isotope Separation. Held in Amsterdam, April 23–27, 1957. Edited by J. KISTEMAKER, J. BIGELEISEN and A. O. C. NIER. North-Holland Publishing Company, Amsterdam, 1958. 702 pp., 112s.

THIS first international symposium on isotope separation reflects the great expansion of interest in isotopes during the last two decades and is notable for the release of a great deal of hitherto restricted

technological information on particular isotopes of importance to the atomic energy industry. Consequently a large part of the conference proceedings is taken up with chemical engineering papers on the design and development work which led to the large scale multistage isotope separation processes used for the production of ^{235}U and, on a smaller scale, of D, Li, ^{10}B, ^{13}C, ^{15}N and ^{18}O.

The proceedings thus provide an excellent review of chemical exchange, distillation, and diffusion, and deal thoroughly with the criteria for the selection of processes, their fundamental principles and the practical techniques.

Other methods of isotope separation which may have particular advantages in special cases or which have been developed as possible alternatives to these processes used on the larger scale are also dealt with. Thus there is much quite detailed information about gas chromatography, ion exchange and thermal diffusion, while accounts are given of the applications of these methods and of the relatively new methods of electromigration, gas centrifuge, and jet diffusion to a variety of elements including Li, Mg, S, Cl and Br and a number of common metals as well as those listed above.

One of the nine parts of the book covers the electromagnetic separator which, on account of its large separation factor and versatility, provides isotopes of all the elements but in small amounts. Several papers in this section deal with the recent work on the provision of the Pu isotopes.

The main interest of those who attended the symposium was in the techniques of separation, but most scientists not directly concerned in this specialization will be more interested in the availability of particular isotopes and their applications in many fields of work. These readers will learn from this book that any naturally occurring isotope of almost all the elements can now be obtained in an enriched state.

The inorganic chemist will be interested in the details of the many interesting processes and reactions with which he is already familiar such as distillation, ion exchange, electromigration, partition and centrifugation. Diffusion is perhaps a rather less familiar process in the laboratory but is noteworthy by its successful large scale application. The more academically inclined may well be led to consider the possibilities of studying isotopic effects in a wide range of nuclei. Thus the new developments have notably increased the range of interest of workers in the field of inorganic chemistry which already has been greatly expanded by other developments in nuclear science.

The book, considered as a work of reference, has the defect of lacking a general subject index, while some of the papers, due to the strict timetable set by the editors in their entirely creditable and successful effort to achieve early publication of the conference proceedings, are only printed in abstract form. As some compensation there is a very detailed contents list. Most of the sixty-three papers are in English, fourteen being in the other official conference languages—French and German.

The book is well illustrated and produced and constitutes not only an essential work of reference but also a worthy record of a memorable conference.

M. L. SMITH

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V. Y. LABATON: The fluorides of uranium—IV. Kinetic studies on the fluorination of uranium tetrafluoride by chlorine trifluoride.

V. Y. LABATON and K. D. B. JOHNSON: The fluorides of uranium—III. Kinetic studies of the fluorination of uranium tetrafluoride by fluorine.

F. K. LOTGERING: Topotactical reactions with ferrimagnetic oxides having hexagonal crystal structures—I.

T. D. SMITH: The salts of organic phosphorus acids—I. The infra-red spectra of salts of di-*n*-butyl phosphate.

D. G. TUCK and G. A. WELCH: The properties of inorganic compounds in organic solvents—II. The ion exchange reactions of quadrivalent plutonium in diethylene glycol dibutyl ether.

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E. G. PROUT and M. J. SOLE: The thermal decomposition of irradiated silver permangate.

C. R. GUILIANO and H. M. MCCONNELL: Rate of electron transfer between vanadium (V) and vanadium (IV) by nuclear magnetic resonance.

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K. W. R. JOHNSON: The preparation of high-purity plutonium metal.

R. F. BARNES, D. J. HENDERSON, A. L. HARKNESS and H. DIAMOND: The alpha and electron capture partial half-lives of ^{243}Am.

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E. HESFORD, E. JACKSON and H. A. C. MCKAY: Tri-*n*-butyl phosphate as an extracting agent for inorganic nitrates—VI. Further results for the rare earth nitrates.

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D. F. BOWERSOX and J. A. LEARY: The solubility of plutonium in mercury.

R. F. WILSON and L. J. BAYE: Thermogravimetric pyrolosis of 1,2,3-benzotriazole compounds of osmium.

K. L. HALL and W. W. MEINKE: Determination of (*d*, alpha) reaction cross-section.

Y. K. GUPTA and S. GHOSH: The silver catalysed oxidation of manganous ion by persulphate.

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E. RICHARDSON: Molybdic acid and its organic complexes—II. Complex formation between molybdic acid and polyhydroxy organic compounds.

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C. B. AMPHLETT, L. A. MCDONALD, J. S. BURGESS and J. C. MAYNARD: Synthetic inorganic ion-exchange materials—III. The separation of rubidium and caesium of zirconium phosphate.

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P. S. GENTILE, L. H. TALLEY and T. J. COLLOPY: Some evidence for the presence of uranic acid in uranium trioxide—Water systems.

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D. A. BROWN: Organometallic complexes—III. On the possible existence of metal–organic complexes containing hetero-atoms.

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W. P. GRIFFITH, F. A. COTTON and G. WILKINSON: The infra-red spectrum of $K_4[Ni(CN)_3CO]_2$.

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M. A. FINEMAN and R. DAIGNAULT: Electronegativates calculated using a modification of Pauling's equation.

T .V. HEALY, J. KENNEDY and G. M. WAIND: The extraction of nitrates by polyphosphorylated reagents—II. The relat'ive extraction rates of uranyl, cobaltous and sodium nitrates with phosphate esters.

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D. HALL and G. N. WALTON: Chemical effects in fission recoil—IV. The efficiency of recoiling atom in the decomposition of potassium nitrate.

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THE ALPHA AND ELECTRON CAPTURE PARTIAL HALF-LIVES OF ^{242}Am*

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Abstract—The partial α-half-life and partial electron capture half-life of the ground state of ^{242}Am were measured at 32,000 ± 1600 years and 960 ± 50 years, respectively. The α-half-life of ^{243}Am was found to be 7720 ± 160 years, in agreement with the more precise specific activity measurements of WALLMAN *et al.* The estimated errors are based on standard deviations.

THE long lived ground state of ^{242}Am is unique in decaying measurably by β-emission, electron capture, and α-emission. The partial β^--half-life has been measured[1] at 182 ± 8 years. In this work, the partial electron capture and α-half-lives were obtained by measuring the rate of production of ^{242}Pu and ^{238}Np in a sample whose ^{242}Am content had been determined mass spectrometrically. The mass spectrometric analyses together with the α-pulse-height analyses yielded the α-half-life of ^{243}Am.

α-*Half-life of* ^{243}Am

Extensive irradiation of plutonium in the Materials Testing Reactor produced milligram quantities of americium. The mass and activity ratios shown in Table 1

TABLE 1.—COMPOSITION OF AMERICIUM

	Atom (%) (N)	% by Activity (A)
^{241}Am	0·469 ± 0.006	7·36 ± 0.12
^{242}Am	0·0048 ± 0·0002	
^{243}Am	99·526 ± 0·006	92·64 ± 0·12

were obtained by mass spectrometric and α-pulse-height analyses of portions of the americium. The α-half-life of ^{243}Am can be calculated from these data, using the formula

$$T_{\frac{1}{2}}(^{243}\text{Am}) = T_{\frac{1}{2}}(^{241}\text{Am}) \times \frac{^{243}\text{N} \times {}^{241}\text{A}}{^{241}\text{N} \times {}^{243}\text{A}}$$

where ^{243}N/^{241}N is the mass ratio and ^{241}A/^{243}A is the α-activity ratio as given in Table 1. The value used for the α-half-life of ^{241}Am was 458·1 ± 0·5 years.[2] The ^{243}Am half-life obtained from these data is 7720 ± 160 years, in good agreement with the more precise value of WALLMAN *et al.*[3] of 7951 ± 48 years. Two other unpublished

* Based on work performed under the auspices of the U.S. Atomic Energy Commission.

[1] D. J. HENDERSON, *J. Inorg. Nucl. Chem.* To be published.
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recent measurements similar to this one gave 7600 years.[4,5] Earlier values of 10^4 years[6] and of 8800 $\pm$ 600 years[7] have been reported. The value 7951 years will be used for calculation hereinafter. The stated errors in this paper are based on standard deviation.

α-*Half-life of* ^{242}Am

The modes of decay of the nuclides in the americium sample are shown in Fig. 1. The ^{238}Np in the sample would be difficult to measure directly because of the million-fold more activity of ^{239}Np present. The ^{238}Pu in the sample arises principally from ^{242}Am β-decay and subsequent ^{242}Cm α-decay, so it would not be useful in obtaining the ^{242}Am α-half-life. A meaningful measurement can be obtained, however, by extracting the neptunium from several milligrams of americium, purifying it from both americium and plutonium, allowing it to decay into plutonium, and examining the ^{238}Pu to ^{239}Pu ratio by α-pulse analysis.

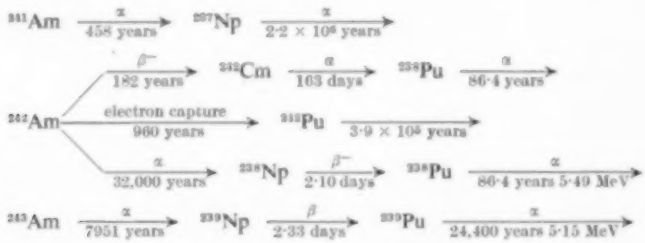

FIG. 1.—Modes of decay of nuclides in the americium sample.

The americium, in equilibrium with its short lived neptunium daughters, was separated from the neptunium by elution with 10 M HCl–0·05 M HNO_3 from a Dowex A-1 ion exchange column. This also purified the americium of plutonium and served as a cleanup step in the ^{242}Am electron capture half-life determination. The plutonium was removed from the column with NH_4I and $N_2H_2 \cdot 2HCl$ in 10 M HCl and the residual neptunium eluted with 2 M HCl.

The neptunium was further purified from americium and plutonium by thenoyltrifluoroacetone (TTA) extraction,[8] followed by a cation exchange procedure. Neptunium (VI) is reduced to the (V) state by Dowex 50 and elutes before uranium with 2 M HNO_3,[9] while uranium elutes before plutonium under the same conditions;[10] hence the neptunium is eluted much earlier than the plutonium. The neptunium was put through another TTA extraction and mounted on a platinum plate for α-pulse analysis. After allowing several weeks for the complete decay of neptunium to plutonium, the ratio of the ^{239}Pu to ^{238}Pu activities was found in two determinations to be 326 $\pm$ 16 and 334 $\pm$ 10. These values include the small (less than 2 per cent)

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corrections for the lack of complete equilibrium between the neptunium and the americium and for the slight difference in decay of the two neptunium isotopes during the period from the initial separation of the neptunium from americium to the final separation of the plutonium and neptunium.

The ^{242}Am partial α-half-life is given by

$$T_{\frac{1}{2}}(^{242}\text{Am}) = T_{\frac{1}{2}}(^{243}\text{Am}) \frac{T_{\frac{1}{2}}(^{238}\text{Np})\ T_{\frac{1}{2}}(^{239}\text{Pu})\ ^{239}\text{A}\ ^{242}\text{N}}{T_{\frac{1}{2}}(^{239}\text{Np})\ T_{\frac{1}{2}}(^{238}\text{Pu})\ ^{238}\text{A}\ ^{243}\text{N}}$$

The half-lives[11] of ^{243}Am, ^{239}Pu, ^{238}Pu, ^{238}Np and ^{239}Np are 7951 years, 24400 years, 86·4 years,[12] 2·1 days and 2·33 days respectively; ^{242}N and ^{243}N are the mole per cent of ^{242}Am and ^{243}Am from Table 1. The half-life obtained from these data (allowing for the slight decay of ^{242}Am) is 32000 ± 1600 years. The only previous value reported is ca. 10^4 years.[6]

Electron capture half-life of ^{242}Am

The above purified sample of americium was set aside for one to two months, after which the neptunium and plutonium were separated and allowed to stand until the neptunium had all decayed to plutonium. The plutonium was then purified and examined by mass spectrometer. Two successive determinations of plutonium from the americium sample yielded ^{239}Pu to ^{242}Pu ratios of 2561 ± 80 and 2478 ± 62. The agreement of these two values demonstrates that none of the ^{242}Pu originally in the sample remained. The ^{242}Am electron capture partial half-life calculated from the plutonium and americium mass spectrometric measurements is 960 ± 50 years.

This value compares with an earlier determination[13,14] of 850 years for the *K* electron capture half-life made by comparing the plutonium *K* X-ray activity with the 60 keV γ-activity of ^{241}Am in a sample containing both ^{241}Am and ^{242}Am. The highly forbidden ($\log_{10}$ft ~ 11·4) beta transition in ^{242}Am implies an equally highly forbidden electron capture transition since the decay energies are almost equal (590 keV and 660 keV) and the states to which they decay in ^{242}Cm and ^{242}Pu are almost identical. From this, one would expect a substantial contribution from *L* electron capture which would be included in the mass spectrometric determination, but was not reported in the earlier work.

SUMMARY

From reference 1 and this work, the total half-life of the ^{242}Am ground state is 152 ± 7 years. The α-, β-, and electron capture branches are 0·476 ± 0·014, 83·6 ± 0·8 and 15·9 ± 0·3 per cent respectively. All of these determinations share the same ^{242}Am content measurement, and the error from this source is not included in the branching ratio.

[11] Half-lives taken from J. M. Hollander, I. Perlman and G. T. Seaborg, *Rev. Mod. Phys.* **25**, 469 (1953) except where otherwise noted.
[12] D. C. Hoffman, G. P. Ford and F. O. Lawrence, *J. Inorg. Nucl. Chem.* **5**, 6 (1957).
[13] H. Jaffe, *University of California Report, UCRL*-2537 (1954).
[14] R. W. Hoff, H. Jaffe, T. O. Paasel, F. S. Stephens, Jr., E. K. Hulet and S. G. Thompson, *Phys. Rev.* 1403 (1955).

J. Inorg. Nucl. Chem., 1959, Vol. 9, pp. 108 to 112. Pergamon Press Ltd. Printed in Northern Ireland

THE SOLUBILITY OF PLUTONIUM IN MERCURY*

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Abstract—The solubility of plutonium in mercury has been measured throughout the temperature range of 20°–325°C. By analogy with the uranium–mercury system, it is assumed that the composition of the solid phase is $PuHg_4$. The solubility, which increases from 2·10 g Pu/l. Hg at 20°C to 85·7 g Pu/l. Hg at 325°C, fits the equation $d(\log N_1)/d(1/T) = -\Delta H/2{\cdot}303R$, where N_1 is the mole fraction of $PuHg_4$ in solution, T is the temperature in degrees Kelvin, ΔH is the heat absorbed when one mole of $PuHg_4$ is dissolved in an infinitely large quantity of saturated solution at temperature T, and R is the gas constant. ΔH is 4·33 kcal/mole in this temperature range.

RECRYSTALLIZATION from the solvent mercury has been proposed[1] as a high temperature reprocessing method for spent fission reactor fuels. Although the phase diagram for the uranium–mercury system has been reported, information pertaining to the plutonium–mercury system is very limited. The compounds $PuHg_4$ and $PuHg_3$ are reported to be isostructural with UHg_4 and UHg_3[2] but the existence of the plutonium analog of UHg_2 has not been established. The solubility of plutonium in mercury at room temperature has been reported by WHITE[3] to be equivalent to 2·2 g plutonium per l. mercury, but the variation in solubility with temperature has not been investigated.

In this study the solubility of plutonium in mercury has been determined as a function of temperature in the 20°–325°C range. No measurements were attempted at temperatures above the normal boiling point of mercury.

EXPERIMENTAL

The reaction vessel and vacuum system used in this study are shown in Fig. 1. The apparatus was designed for equilibrating and sampling under an inert atmosphere in order to eliminate oxidation of the plutonium by air.

In a typical experiment, 70 ml of triple distilled mercury was outgassed in the reaction vessel at 250°C, then cooled to room temperature. The reaction vessel was then filled with helium, and approximately 10 g of freshly machined, shiny plutonium turnings were added through joint *A* against a back-flow of helium. The purity of the plutonium was 99·8 wt. per cent. Joint *A* was resealed and the reaction vessel was again evacuated and filled with helium several times. The plutonium–mercury mixture was then held at 250°–300°C for 24 hr under a helium atmosphere, during which time the reaction vessel was shaken periodically by hand. After this preliminary equilibration, the temperature of the reaction vessel was adjusted to the desired value, and the liquid phase was again agitated periodically by shaking, then sampled at temperature.

The liquid phase was sampled periodically by evacuating the lower region of the reaction vessel through stopcock *D*, thereby forcing 3–10 ml of mercury solution through the fritted disc. This sample was transferred into a weighed 50 ml volumetric flask connected at *C*, then weighed at room temperature. The sample volume at the filtration temperature was computed from the density of

* Work done under the auspices of the Atomic Energy Commission.

(1) B. H. MORRISON and R. E. BLANCO, *The Hermex Process for Metal Decontamination. ORCF*-56-151 (1956).
(2) A. S. COFFINBERRY and M. B. WALDRON, *The Physical Metallurgy of Plutonium, Progress in Nuclear Energy*, Series V, Vol. 1, p. 401. Pergamon Press, London (1956).
(3) A. G. WHITE, *The Preparation of Plutonium Amalgam and its Reaction with Dilute Hydrochloric Acid. AERE C/R*-1468 (1954).

mercury at that temperature.[4] The plutonium was then leached from the mercury by contacting with 25 ml concentrated hydrochloric acid for 24 hr. This plutonium chloride solution was filtered and the mercury residue was washed with hydrochloric acid. The plutonium solution and washes were then diluted to 50·00 ml and aliquots were analysed by radio-assay for plutonium content.

In a separate series of experiments, it was demonstrated that leaching for 24 hr with concentrated hydrochloric acid removed essentially all of the plutonium from the mercury, regardless of the initial

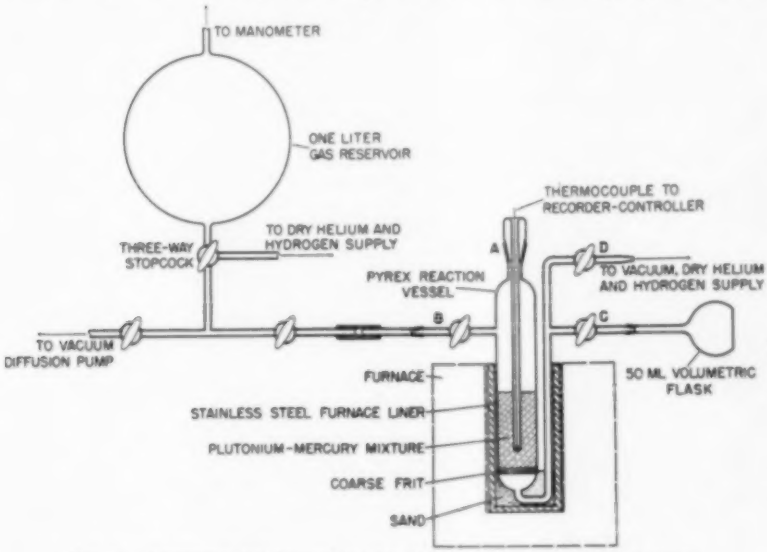

FIG. 1.—Apparatus for determining the solubility of plutonium in mercury.

plutonium concentration. In these experiments each mercury residue that had been leached was completely dissolved in nitric acid. Radio-assay of this solution indicated that less than 1 per cent of the plutonium had remained in the mercury phase.

The accuracy of the plutonium analysis is estimated to be about 1 per cent after correcting for americium content and plutonium specific activity. The estimated error in temperature measurement during sampling corresponds to a possible error of approximately 1–2 per cent in the solubility determination.

RESULTS

The apparent solubility of plutonium in mercury is shown as a function of time at temperature in Table 1. These results indicate that reasonably constant solubility values were reached after about 20 hr at temperature. Moreover, the value obtained after 22 hr at 260°C was independent of the direction from which the equilibrium temperature was approached. Therefore, each solubility measurement was determined by taking samples after approximately 16 and 22 hr at temperature.

Because the solubility computed from these two samples normally was in agreement within the limits of experimental error, the average value was taken as the solubility.

The solubility of plutonium in mercury is shown as a function of temperature in Table 2. Except where noted, the solubility measurement at each temperature is the result of at least two separate experiments, i.e. separate loadings and equilibrations of plutonium and mercury in the reaction vessel.

[4] *Handbook of Chemistry and Physics* (39th Ed.) p. 1995. Chemical Rubber Publishing Company, New York (1957).

DISCUSSION

By analogy with the uranium–mercury system, the solubility of plutonium in mercury in the temperature range studied probably corresponds to the following equilibrium:

$$PuHg_4 \text{ (solid)} = PuHg_4 \text{ (in saturated solution)} \quad (1)$$

It can be shown by thermodynamic argument that at constant pressure

$$\frac{\partial(\ln N_1)}{\partial(1/T)} + \frac{\partial(\ln \gamma_1)}{\partial(1/T)} = -\frac{\Delta H}{R} \quad (2)$$

TABLE 1.—THE SOLUBILITY OF PLUTONIUM IN MERCURY AS A FUNCTION OF TIME

Temperature (°C)	Time at temp (hr)	"Solubility" g/l.
24	6	2·85
	18	2·56
	22	2·60
	68	2·64
150	5	14·3
	15	20·0
	21	20·1
260	2	19·2
	6	23·8
	22	58·6
	23	58·8[a]

[a] Approached from a temperature lower than 260°C. All other measurements approached from a temperature of 300°C.

TABLE 2.—THE SOLUBILITY OF PLUTONIUM IN MERCURY AS A FUNCTION OF TEMPERATURE

Temperature (°C)	Pu solubility (g/l. Hg)	Pu atomic fraction × 10^3
21	2·10	0·131
24	2·59	0·161
50	4·10	0·255
100	9·95	0·625
150	19·8	1·26
190	28·5	1·82
200	29·6	1·90
225[a]	42·8	2·75
260	58·8	3·80
280[a]	64·9	4·21
300	76·1	4·96
325[a]	85·7	5·61

[a] Based on one experiment.

where N_1 is the mole fraction of $PuHg_4$ in solution, γ_1 is the $PuHg_4$ rational activity coefficient, T is the absolute temperature, R is the gas constant, and ΔH is the heat absorbed when one mole of $PuHg_4$ is dissolved in an infinite quantity of saturated

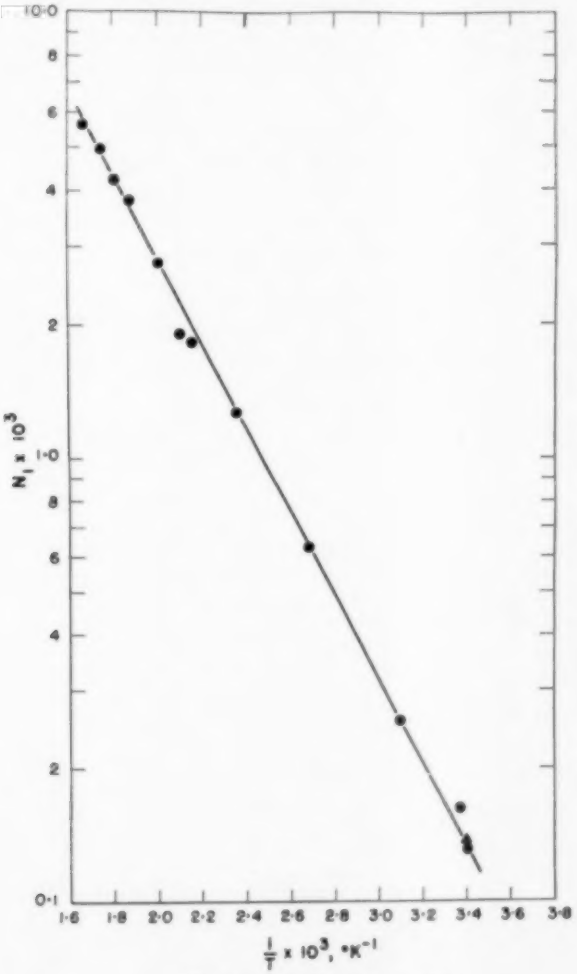

FIG. 2.—Plot of log N_1 vs. $1/T$.

solution at temperature T. If γ_1 does not change significantly with temperature, equation (2) may be simplified to

$$\frac{\partial(\log N_1)}{\partial(1/T)} = \frac{-\Delta H}{2{\cdot}303R} \tag{3}$$

From equation (3) it may be seen that a plot of log N_1 vs. $1/T$ should be linear if ΔH is essentially constant over the given temperature range. The validity of equation (3) is demonstrated in Fig. 2, which is a plot of the solubility data in Table 2. The value of ΔH computed from the slope of the line in Fig. 2 is 4330 cal/mole.

The room temperature solubility value reported by WHITE (shown as a solid bold triangle in Fig. 2) is in good agreement with the results obtained in this study if room temperature is assumed to be approximately 22°C.

Acknowledgements—We are indebted to the analytical group under the direction of C. F. METZ for radio-analyses, and to W. J. MARAMAN for consultation during this study.

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TOPOTACTICAL REACTIONS WITH FERRIMAGNETIC OXIDES HAVING HEXAGONAL CRYSTAL STRUCTURES—I

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Abstract—A new method is described for the preparation of polycrystalline materials with oriented crystals by reaction of the oriented grains of a strongly anisotropic ferrimagnetic with non-oriented grains of usually non-magnetic components. Using this type of reaction, for which the name "topotactical (or "topotaxial") reaction" is proposed, oriented samples of $Ba_3Co_\delta Zn_{2-\delta}Fe_{24}O_{41}$, $BaCo_\delta Zn_{2-\delta}Fe_{16}O_{27}$, $Ba_2Zn_2Fe_{12}O_{22}$ and $BaCo_\delta Ti_\delta Fe_{12-2\delta}O_{19}$, which have related hexagonal crystal structures, have been prepared as well as some ferrites having the cubic spinel structures.

THE present investigation deals with reactions between oxides of the system BaO–MeO–Fe_2O_3 in which Me represents a divalent metal like Mn, Fe^{II}, Co, Zn etc. In this system ferrimagnetic compounds occur. We will briefly review some crystallographic and magnetic properties of these materials, which are described by JONKER *et al.*[1]

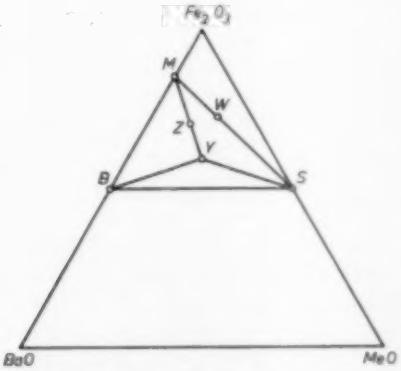

FIG. 1.—Composition diagram of the system BaO–MeO–Fe_2O_3. $BaFe_{12}O_{19}$(*M*), $Ba_3Me_2Fe_{24}O_{41}$(*Z*), $Ba_2Me_2Fe_{12}O_{22}$(*Y*), $BaMe_2Fe_{16}O_{27}$(*W*), $MeFe_2O_4$(*S*) and $BaFe_2O_4$(*B*).

The most important compounds in the BaO–MeO–Fe_2O_3 system (Fig. 1) are $BaFe_{12}O_{19}$ (denoted by *M*), $Ba_3Me_2Fe_{24}O_{41}$ (Me_2Z), $Ba_2Me_2Fe_{12}O_{22}$ (Me_2Y) $BaMe_2Fe_{16}O_{27}$(Me_2W), $MeFe_2O_4$ (*S*) and $BaFe_2O_4$ (*B*). *M*, Me_2Z, Me_2Y and Me_2W have closely related hexagonal crystal structures,[1,2] which can be considered to be composed of layers with spinel structure (a cubic [111] direction of spinel being parallel to the hexagonal axis) and of layers (with a characteristic structure) that

[1] G. H. JONKER, H. P. J. WIJN and P. B. BRAUN, *Philips Techn. Rev.* **18**, 145 (1956); *Proc. Instn. Electr. Engrs.* B **104**, *Supplement*, 249–254 (1957).
[2] P. B. BRAUN, *Philips Res. Rep.* **12**, 491 (1957).

contain the Ba^{2+} ions. The two types of layers lie perpendicular to the hexagonal axis and alternate in the c-direction. Combinations of spinel layers with a thickness of 6·9 and 11·5 Å with two types of layers containing Ba (with a thickness of 4·6 and 6·9 Å) give a series of structures to which M, Me_2Z, Me_2Y and Me_2W belong. The hexagonal unit cells of all these lattices have approximately equal a-edges whereas the c-edges are different. S has the well-known spinel structure; the crystal structure of B is not known.

The most important magnetic property of the hexagonal ferrimagnetic compounds is the fact that the crystalline anisotropy energy E_K is mainly determined by, and strongly dependent on, the angle θ between the direction of the magnetization and the c-axis. To a first approximation the equation:

$$E_K = K_1 \sin^2 \theta$$

holds. If K_1 is positive, the minimum of E_K occurs for $\theta = 0$ or 180°, i.e. a preferential direction for the magnetization is present. In the case of a negative K_1, the minimum occurs for $\theta = 90°$ and the material has a "preferential plane" for the magnetization. M, Me_2Z and Me_2W, except for Me=Co, have a preferential direction, Co_2Z, Co_2W and Me_2Y have a preferential plane for the magnetization, at room temperature.

A complete series of mixed crystals $Co_\delta Me_{2-\delta}Z$ between a compound with a preferential direction (e.g. Zn_2Z) and Co_2Z exist. In such a series K_1 changes from a positive value for $\delta = 0$ to a negative value for $\delta = 1$. For a certain value of δ, K_1 is zero and for a range of compositions around this δ value K_1 is small. A similar behaviour occurs for $Co_\delta Zn_{2-\delta}W$ because K_1 is positive for Zn_2W and negative for Co_2W.

In this laboratory GORTER[3] found a series of materials $BaCo_\delta Ti_\delta Fe_{12-2\delta}O_{19}$ (up to $\delta = 6$), which will be denoted by $Co_\delta Ti_\delta M$. They are isomorphous with $BaFe_{12}O_{19}$ and can be derived from the latter compound by a substitution of $Ti^{IV} + Co^{II}$ for $2Fe^{III}$. For increasing δ, K_1 decreases and passes through zero so that for a certain range of δ the materials have a preferential plane for the magnetization (at room temperature).

For certain purposes polycrystalline materials with crystals of which the c-axes are oriented parallel to each other are desired in order to take the full advantage of the characteristic anisotropy.[4] Samples with such a texture have the same type of magnetic anisotropy as the composing crystals, e.g. for negative K_1 the material has a preferential plane for the magnetization perpendicular to the c-axes. Crystals for which $K_1 > 0$ can be oriented in a static magnetic field, crystals for which $K_1 < 0$, in a rotating magnetic field.[4] (The rotating field has the tendency to orient the preferential planes of the crystals parallel to the plane in which the field rotates.) Well-oriented samples can be obtained by orienting finely ground powders of, e.g., M, Zn_2Z and Zn_2W in static fields and of Co_2Z, Co_2W and Me_2Y in rotating fields higher than approximately 2000 oersteds.

The present work is based on the following experiment, which was performed by Dr. G. H. JONKER in this laboratory. A pellet was pressed from a mixture of $BaFe_{12}O_{19}$ and Fe_3O_4 in the presence of a static magnetic field. Then the strongly anisotropic M

[3] E. W. GORTER, *Proceedings Grenoble Conference on Ferromagnetism* (1958).
[4] A. L. STUYTS and H. P. J. WIJN, *Philips Techn. Rev.* **19**, 209 (1957).

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crystals are oriented with their *c*-axes parallel to the field whereas the weakly anisotropic Fe_3O_4 crystals are not oriented. By heating the mixture in a suitable gas atmosphere the reaction

$$BaFe_{12}O_{19} + 2Fe^{II}Fe_2O_4 \rightarrow BaFe_2^{II}Fe_{16}O_{27}(Fe_2^{II}W)$$

takes place. Dr. JONKER made the interesting observation that the hexagonal $Fe_2^{II}W$ crystals of the polycrystalline reaction product were oriented more or less parallel to the hexagonal *M* crystals in the initial mixture. In other words, the texture of the *M* crystals in the initial mixture was retained in the $Fe_2^{II}W$ crystals.

Such reactions of a strongly anisotropic ferrimagnetic component, whose crystals are oriented in a magnetic field, with other components, whose crystals are not oriented in the field, open up the possibility of a fundamentally new method for the preparation of oriented materials. For these reactions the name "topotactical reactions" or "topotaxial reactions" is proposed (cf. Section 5). As Dr. E. W. GORTER in this laboratory suggested, this new method, in which the anisotropy of the final product plays no part, may be especially important for orienting materials with such a low anisotropy that they cannot be oriented directly in a field.

This paper describes an investigation of the preparation of oriented $Co_\delta Zn_{2-\delta}Z$, $Co_\delta Zn_{2-\delta}W$, $Co_\delta Ti_\delta M$ and $Ni_\delta Zn_{1-\delta}Fe_2O_4$ using topotactical reactions.

1. COMPOSITION OF THE INITIAL MIXTURE AND PREPARATION TECHNIQUE

The composition of the initial mixture for a topotactical reaction was chosen in the following ways.

(a) The initial mixture contains one or more ferrimagnetic components (like *M*, Zn_2Z, etc.) that are oriented in a field, and non-orientable components in such quantities that the gross composition is equal to the composition of the desired final product.

For the composition of Me_2Z, Me_2W or Me_2Y numerous compositions of initial mixtures can be chosen with the aid of the BaO–MeO–Fe_2O_3 diagram (Fig. 1). A mixture of *M*, BaO and MeO can have all gross compositions within the triangle M–BaO–MeO, which contains the compositions of Me_2Z and Me_2Y. For example $Co_\delta Zn_{2-\delta}Z$ can be prepared from *M*, BaO, CoO and ZnO:

$$2BaFe_{12}O_{19}\uparrow + BaO + \delta CoO + (2-\delta)ZnO \rightarrow Ba_3Co_\delta Zn_{2-\delta}Fe_{24}O_{41}$$

(Materials oriented by a static or by a rotating field are denoted by the symbols $\uparrow$ or $\perp$, respectively.)

For the preparation of $Co_\delta Ti_\delta M$, mixtures of *M*, Me_2Z, Me_2W or Me_2Y with additions containing TiO_2 can be used, e.g.

$$(\delta/2)Ba_3Co_2Fe_{24}O_{41}\perp + (1-3\delta/2)BaO + \delta TiO_2 + (6-7\delta)Fe_2O_3 \rightarrow BaCo_\delta Ti_\delta Fe_{12-2\delta}O_{19} \text{ (for } \delta < \tfrac{8}{5})$$

(b) In the starting mixture a component containing Fe^{II} is present and oxidation takes place during the reaction, e.g.

$$\tfrac{4}{3}BaFe_2^{II}Fe_{16}O_{27}\uparrow + \tfrac{5}{3}BaCO_3 + 2CoCO_3 + \tfrac{2}{3}O_2 \rightarrow Ba_3Co_2Fe_{24}O_{41} + \tfrac{11}{3}CO_2$$

Method (a) is the more general and more practical method. Method (b) has the disadvantage that the preparation of a material containing Fe^{II} is often laborious.

The preparation of the materials was carried out as follows. The initial mixture was ground for 8 hr under ethanol in a vibration mill. From a wet slurry of the powder a pellet was pressed in the presence of a static field of 8000 oersteds or a rotating field of 3000 oersteds. The pellet was heated slowly in an oxygen atmosphere, kept at 1250°C for a certain time and furnace cooled.

2. THE ESTABLISHMENT OF A TEXTURE AND THE ESTIMATION OF THE DEGREE OF ORIENTATION

The texture of an oriented, polycrystalline material is defined exactly by a distribution function giving the fraction of material with crystals having *c*-axes that make a certain angle with the direction of orientation, as a function of the angle. The texture cannot be described exactly by a single parameter because in general such a distribution function will be determined by more than one constant. Since the measurements of distribution functions for a series of samples is too cumbersome, we have confined ourselves to establishing a texture and estimating the degree of orientation semi-quantitatively in the following ways.

(a) *X-ray diagram.* When X-ray beams are reflected from the planes parallel to the basal plane of an ideally oriented sample, then all (*hkl*) reflections except the (00*l*) reflections disappear from the X-ray diagram. In the X-ray diagrams of incompletely oriented materials the (*hkl*) reflections still occur. The ratio of the intensities of the (00*l*) and (*hkl*) reflections increases with improving orientation. The degree of orientation was estimated by comparing the X-ray diagrams of the samples with that of non-oriented material with the same crystal structure in the following way. (The influence of the metal chosen for Me in Me_2Z, Me_2W and Me_2Y on the X-ray intensities is very weak and can be neglected.)

From the X-ray diagrams the sum of the intensities of the (00*l*) reflections and the sum of the intensities of all (*hkl*) and (00*l*) reflections (which occur in a certain range of θ values) were obtained and the ratio of the two sums was calculated for an oriented sample (value p) and for the non-oriented material (value p_0). For an increasing degree of orientation p increases from the value p_0 for the non-oriented sample to the value 1·0 for an ideally oriented sample so that the quantity $f = (p - p_0)/(1 - p_0)$ increases from 0 (non-oriented) to 1·0 (ideally oriented). The quantity f, which may be considered as a measure of the degree of orientation (although of course f does not describe the orientation distribution), was taken as a quality factor for the orientation.

The X-ray diagrams of the non-oriented samples were obtained with the aid of a high-angle Norelco spectrometer. By this means sufficient resolution of the lines was obtained to enable p_0 to be determined with reasonable accuracy. The p values for the oriented samples were estimated from X-ray diagrams in which the (00*l*) reflections were partially overlapped by (*hkl*) reflections. This procedure, however, is increasingly inaccurate for decreasing degree of orientation so that low values of f are correspondingly inaccurate. Therefore, the f values are tabulated to one or two decimal places for f smaller or larger than 0·8, respectively.

The orientation was further qualified as "very good" if the reflections (1.0.16) for Me_2Z, (1.0.11) for Me_2W and (1.0.7) for M were absent or weak. (These being the reflections that vanish last of all non-basal reflections for increasing degree of orientation.) The term "good" was used if the non-basal reflections apart from the (*h*0*l*)

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reflections mentioned above, are weak, and the terms "moderate" and "poor" if the (00*l*) reflections are respectively, considerably or only slightly stronger, than those for non-oriented materials whereas several strong non-basal reflections are present.

(b) *Initial permeabilities $\mu_\parallel$ and $\mu_\perp$.* $\mu_\parallel$ and $\mu_\perp$ are defined as the initial permeabilities at low frequency measured in fields $H_\parallel$ and $H_\perp$, parallel or perpendicular to the direction of the *c*-axes of an oriented sample. If the magnetization is caused by rotation processes then the following behaviour is expected for ideally oriented material.

For large and positive values of K_1, the spontaneous magnetization vectors lie in directions parallel or anti-parallel to the *c*-axes which are both preferential directions for the magnetization. A weak field $H_\perp$ (perpendicular to the magnetization) causes rotations of the magnetization vectors, but only over small angles because the vectors are tightly bound to the preferential direction. Therefore $\mu_\perp$ differs only slightly from unity. A field $H_\parallel$ parallel to the magnetization causes no rotation at all so that $\mu_\parallel = 1$.

For large and negative values of K_1, the magnetization vectors point in directions lying in the preferential plane, which is perpendicular to the *c*-axes. $H_\parallel$ causes rotations of the vectors out of the plane, but only over small angles as a consequence of tight binding of the magnetization in the plane. Therefore $\mu_\parallel$ is small. In the plane, however, the rotation of the magnetization is practically free[1] so that a field $H_\perp$ causes rotations over relatively large angles. Then $\mu_\perp$ is large.

It is evident that for non-oriented materials $\mu_\perp$ and $\mu_\parallel$ are equal. For incompletely oriented materials with a positive K_1 the difference between $\mu_\perp$ and $\mu_\parallel$ is small, $\mu_\perp$ and $\mu_\parallel$ being both small. For incompletely oriented materials with a negative K_1, $\mu_\perp$ can be considerably larger than $\mu_\parallel$, the difference becoming larger for an increasing degree of orientation.

$\mu_\perp$ and $\mu_\parallel$ were calculated from the self-induction of a coil with a cube-shaped core of the oriented material, which was placed in a yoke of material with a permeability larger than 1000. The self induction was measured at 2 Kc/s with the aid of a Maxwell bridge.

(c) *Orientation of a sample in a magnetic field.* A field exercises on an oriented sample a torque that has the tendency to orientate the sample with a preferential direction of magnetization parallel to the field. From the behaviour of a sample in a field the presence of a texture can be shown and the sign of K_1 can be found.

(d) *Microscopic investigation.* Since the hexagonal crystals in the polycrystalline samples usually have the shape of flat plates, which are parallel to the basal planes, photomicrographs of surfaces parallel and perpendicular to the *c*-axes of oriented material give an impression of the texture. The crystal boundaries were observed on polished surfaces that were etched with hydrochloric acid.

(e) *Shrinkage.* During sintering, oriented samples show a greater shrinkage in the direction of the *c*-axes than in the direction perpendicular to it.

3. EXPERIMENTAL RESULTS

$Co_\delta Zn_{2-\delta}Z$. Five different reactions I–V, Table 1, were carried out for the preparation of $Co_\delta Zn_{2-\delta}Z$. The samples were fired 3 or 16 hr at 1250°C in an oxygen atmosphere. From the X-ray diagrams it was concluded that the materials prepared by the reactions II, III and IV, were pure (i.e. contained at most traces of a second

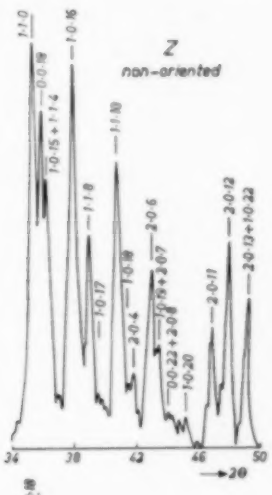
TABLE 1.—TO TOPOTACTICAL REACTIONS CARRIED OUT FOR THE PREPARATION OF $Co_\delta Zn_{2-\delta}$ = $Ba_2Co_\delta Zn_{2-\delta}Fe_{24}O_{41}$, $Co_\delta Zn_{2-\delta}W = BaCo_\delta Zn_{2-\delta}Fe_{16}O_{27}$, $Co_\delta Ti_\delta M = BaCo_\delta Ti_\delta Fe_{12-2\delta}O_{19}$ and $MeFe_2O_4$

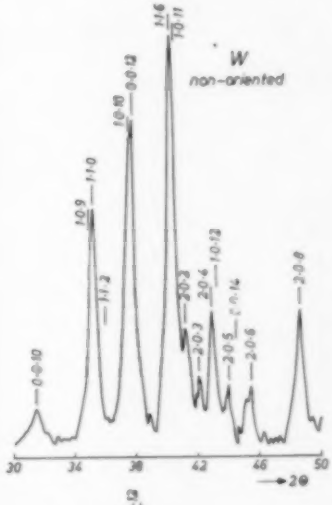
MEANING OF SYMBOLS: $M = BaFe_{12}O_{19}$; $Me_2Y = Ba_2Me_2Fe_{12}O_{22}$; $\uparrow$ and $\perp$ oriented in a static or rotating magnetic field, respectively

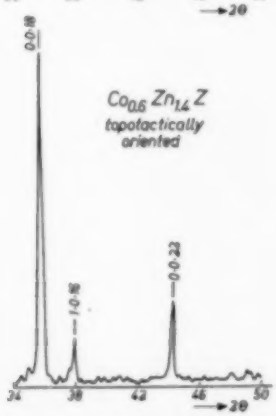
No.	Reaction equation	Orientation concluded from the X-ray diagram (see Section 2a)
I	$2M\uparrow + BaCO_3 + \delta CoCO_3 + (2-\delta)ZnO \rightarrow Co_\delta Zn_{2-\delta}Z + (1+\delta)CO_2$ ($\delta = 0.5, 0.6, 0.7$)	poor ($f = 0.1$)
II	$\delta M\uparrow + (1-\delta/2)Zn_2Z\uparrow + \frac{1}{2}\delta BaCO_3 + \delta CoCO_3 \rightarrow Co_\delta Zn_{2-\delta}Z + \frac{3}{2}\delta CO_2$ ($\delta = 0.5, 0.6, 0.7, 1.0$)	moderate–good $0.3 < f < 0.7$
III	$(1-\delta/2)Zn_2Z\uparrow + \frac{3}{2}\delta BaCO_3 + \delta CoCO_3 + 6\delta Fe_2O_3 \rightarrow Co_\delta Zn_{2-\delta}Z + \frac{5}{2}\delta Co_2$ ($\delta = 0.5, 0.6, 0.7, 1.0$)	good–very good $0.6 < f < 0.91$
IV	$(\delta/2)Co_2Z\perp + (1-\delta/2)Zn_2Y\perp + (1-\delta/2)BaCO_3 + (6-3\delta)Fe_2O_3 \rightarrow Co_\delta Zn_{2-\delta}Z + (1-\delta/2)CO_2$ ($\delta = 0.5, 0.6, 0.7, 1.0$)	good $0.7 < f < 0.8$
V	$\frac{4}{3}Fe_2^{II}W\uparrow + \frac{8}{3}BaCO_3 + 2CoCO_3 + \frac{8}{3}O_2 \rightarrow Co_2Z + \frac{11}{3}CO_2$	moderate ($f = 0.2$)
VI	$M\uparrow + \delta CoCO_3 + (2-\delta)ZnO + 2Fe_2O_3 \rightarrow Co_\delta Zn_{2-\delta}W + \delta CO_2$ ($\delta = 0.6, 0.7, 0.8, 1.0$)	good–very good $0.5 < f < 0.89$
VII	$\frac{1}{3}Zn_2Z\uparrow + \delta CoCO_3 + (\frac{4}{3}-\delta)ZnO + 4Fe_2O_3 \rightarrow Co_\delta Zn_{2-\delta}W + \delta CO_2$ ($\delta = 0.6, 0.7, 0.8, 1.0$)	good $0.5 < f < 0.84$
VIII	$\frac{1}{3}Co_2Z\perp + (\delta-\frac{8}{3})CoCO_3 + (2-\delta)ZnO + 4Fe_2O_3 \rightarrow Co_\delta Zn_{2-\delta}W + (\delta-\frac{8}{3})CO_2$ ($\delta = 0.7, 0.8$)	good–very good $0.8 < f < 0.98$
IX	$(1-\delta/6)M\uparrow + \delta/6BaCO_3 + \delta CoCO_3 + \delta TiO_2 \rightarrow Co_\delta Ti_\delta M + \frac{7}{6}\delta CO_2$ ($\delta = 1.1, 1.3, 1.5$)	good–very good $0.5 < f < 0.97$
X	$\frac{1}{3}Co_2Z\perp + \frac{13}{30}CoCO_3 + \frac{1}{5}TiO_2 + \frac{8}{10}TiFe_2O_5 \rightarrow Co_{1.1}Ti_{1.1}M + \frac{13}{10}CO_2$	moderate ($f = 0.3$)
XI	$\frac{10}{11}Fe^{II}_{1.0}Ti_{1.0}M\uparrow + \frac{1}{11}BaCO_3 + CoCO_3 + \frac{1}{11}TiO_2 + \frac{5}{22}O_2 \rightarrow Co_{1.0}Ti_{1.0}M + \frac{13}{11}CO_2$	good ($f = 0.5$)
XII	$\frac{1}{2}Zn_2Z\uparrow + \frac{1}{2}BaCO_3 + ZnO \rightarrow Zn_2Y + CO_2$	poor ($f = 0.2$)
XIII	$Co_2W\uparrow + 5CoCO_3 \rightarrow 7CoFe_2O_4 + BaFe_2O_4 + 5CO_2$	
XIV	$Ni_2W\uparrow + 5ZnO \rightarrow 7Ni_{2/7}Zn_{5/7}Fe_2O_4 + BaFe_2O_4$	
XV	$Zn_2W\uparrow + 5NiCO_3 \rightarrow 7Zn_{2/7}Bi_{5/7}Fe_2O_4 + BaFe_2O_4 + 5CO_2$	

phase) and well oriented. The X-ray diagram of one of the best oriented preparations is given in Fig. 2. Reaction I gave materials that contained contaminations of other phases (M and Me_2Y) and were oriented poorly. Reaction V gave a pure product with a moderate orientation.

In Table 2 the values of $\mu_\parallel$ and $\mu_\perp$ and other data of some preparations are given.







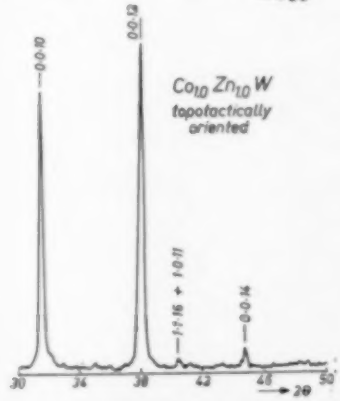


FIG. 2.—X-ray diffraction diagrams of non-oriented and "very well" oriented Me_2Z (CoK_α radiation).

FIG. 3.—X-ray diffraction diagrams of non-oriented and "very well" oriented Me_2W (CoK_α radiation).

The small values of $\mu_\parallel$ and $\mu_\perp$ for a low Co content ($\delta = 0{\cdot}5$) are explained by a positive K_1; the small $\mu_\parallel$ and much higher $\mu_\perp$ values for higher Co contents ($\delta =$ 0·7 or larger) are consistent with a negative K_1 (see Section 2b). The considerable difference between $\mu_\parallel$ and $\mu_\perp$ in the cases of a negative K are on indication of a good orientation. The change from a positive to a negative value of K_1 occurs between $\delta = 0{\cdot}5$ and $\delta = 0{\cdot}7$; thus K_1 passes zero for δ in the neighbourhood of 0·6.

For some samples the texture was microscopically investigated (see Section 2d). Fig. 5 shows the photomicrographics of surfaces parallel and perpendicular to the

c-axes. These pictures confirm the presence of a good orientation, as was concluded from the X-ray diagrams.

$Co_\delta Zn_{2-\delta}W$. These materials were prepared by the three reactions VI, VII and VIII, Table 1. All samples were pure and well or very well oriented (see Fig. 3). From the $\mu_\perp$ and $\mu_\parallel$ values (Table 2) it is seen that K_1 is positive for $\delta = 0{\cdot}6$ and negative for 0·7. Thus K_1 passes through zero for $0{\cdot}6 < \delta < 0{\cdot}7$.

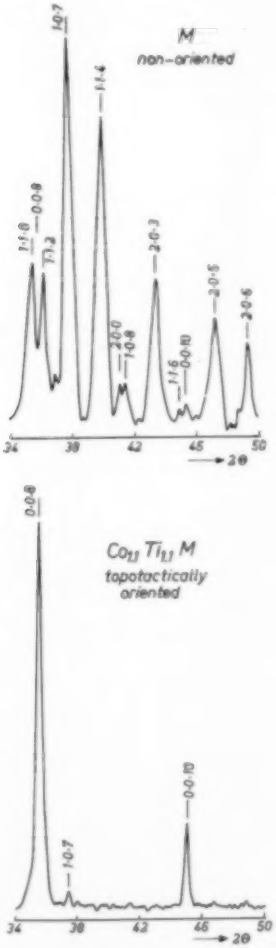


FIG. 4.—X-ray diffraction diagrams of non-oriented M and "very well" oriented CoTiM (CoK_α radiation).

$Co_\delta Ti_\delta M$. The reactions IX and XI gave pure and well or very well oriented materials (see Table 1 and Fig. 4). The final product of reaction X was pure, but moderately oriented. For $\delta = 1{\cdot}1$, $\mu_\perp$ is considerably larger than $\mu_\parallel$ (Table 2), from which it is clear that the material has a preferential plane of magnetization.

Zn_2Y. Reaction XII gave pure, but poorly oriented Zn_2Y.

Me_2Z, Me_2W and $Co_\delta Ti_\delta M$ are formed more easily from mixtures that contain M, Me_2Z or Me_2W as a component than from mixtures of BaO, MeO, Fe_2O_3 and TiO_2. This was shown as follows.

Samples of CoZnZ and CoZnW were prepared from $BaCO_3$, ZnO and Fe_2O_3 and by reactions

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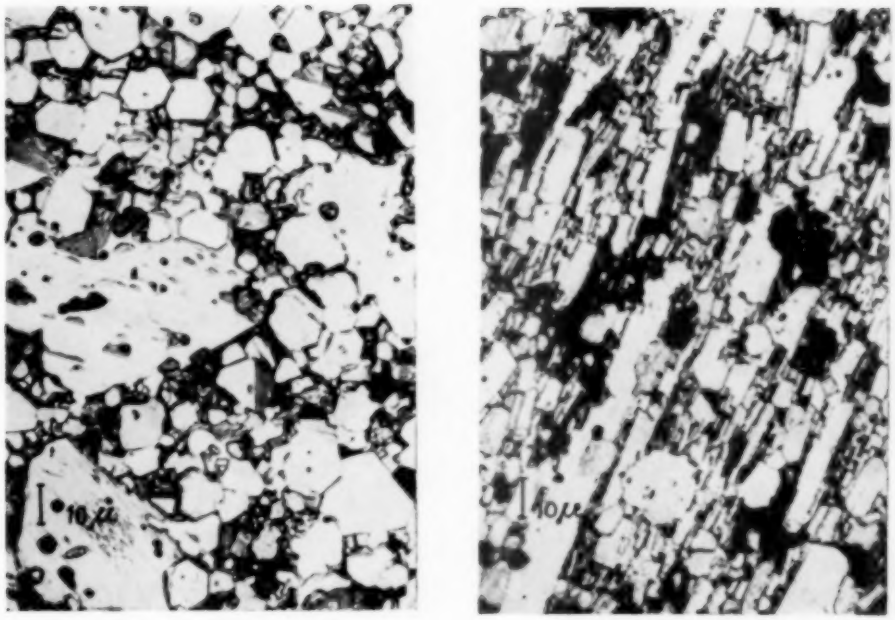

(a) (b)

FIG. 5.—Photomicrographs of topotactically oriented $Co_{0.5}Zn_{0.1}Z$ (density 5·1). (a) Surface parallel to basal plane; (b) Surface parallel to preferential direction of the *c*-axes. The material was qualified as "well oriented" ($f = 0{\cdot}75$) from the X-ray diagram.

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II, III, IV, VI and VII without applying a magnetic field. All samples were fired during 3 hr in oxygen. The reaction products of $BaCO_3$, $CoCo_3$ etc. contained considerable amounts of foreign phases whereas for reactions II, III, IV and VII no second phase and for reaction VI a small amount of foreign phase was found in the final product.

Dr. GORTER found that $Co_\delta Ti_\delta M$ prepared from $BaCO_3$, $CoCO_3$, TiO_2 and Fe_2O_3 is always contaminated by a small amount of $CoFe_2O_4$. This was concluded from the shape of the magnetization vs. temperature curves, which show a tail between the Curie temperatures of $Co_\delta Ti_\delta M$ and $CoFe_2O_4$ (520°C). This tail is practically absent for $Co_\delta Ti_\delta M$ prepared by reaction IX.

TABLE 2.—SPECIFIC WEIGHT d, D.C. SPECIFIC RESISTIVITY r, $\mu_\perp$ AND $\mu_\parallel$ FOR SOME TOPOTACTICALLY ORIENTED $Co_\delta Zn_{2-\delta} Z$, $Co_\delta Zn_{2-\delta} W$ AND $Co_\delta Ti_\delta M$ PREPARATIONS

Composition	Reaction (see Table 1)	Heat treatment (hr—°C)	d	r (Ω cm)	$\mu_\perp$	$\mu_\parallel$	Orientation concluded from the X-ray diagram (see Section 2a) f values between brackets
$Co_{0.5}Zn_{1.5}Z$	II	16–1250°	5·2	10^9	5	8	— —
$Co_{0.6}Zn_{1.4}Z$			5·2	10^9	7	10	good (0·7)
$Co_{0.7}Zn_{1.3}Z$			5·2	10^9	40	14	moderate (0·5)
Co Zn Z		3–1250°	5·1	10^9	32	5	good (0·5)
$Co_{0.5}Zn_{1.5}Z$	III	16–1250°	5·2	10^9	5	9	good (0·6)
$Co_{0.6}Zn_{1.4}Z$			5·2	10^9	8	12	very good (0·91)
$Co_{0.7}Zn_{1.3}Z$			5·2	10^9	41	10	—
Co Zn Z		3–1250°	5·1	10^9	55	4	good (0·7)
$Co_{0.5}Zn_{1.5}Z$	IV	3–1250°	5·1	10^9	4	9	good ($0·7_5$)
$Co_{0.7}Zn_{1.3}Z$			4·8	10^9	23	10	good ($0·7_5$)
Co Zn Z			5·2	10^9	35	5	good (0·7)
$Co_{0.6}Zn_{1.4}W$	VI	3–1250°	4·3	10^7	3_5	7_5	good (0·6)
$Co_{0.7}Zn_{1.3}W$			—	10^8	22	7	good (0·7)
$Co_{0.8}Zn_{1.2}W$			4·3	10^8	20	7	good ($0·7_5$)
Co Zn W			4·3	10^8	12	5	good (0·89)
$Co_{0.8}Zn_{1.2}W$	VII	3–1250°	3·7	10^8	21	5	good (0·6)
Co Zn W			2·8	10^8	8_5	3	good (0·84)
$Co_{0.7}Zn_{1.3}W$	VIII	3–1250°	4·6	10^8	15	2_5	good (0·80)
$Co_{0.8}Zn_{1.2}W$			3·3	10^8	19	5_5	very good (0·86)
$Co_{1.1}Ti_{1.1}M$	IX	3–1250°	4·5	10^8	47	7_5	very good (0·97)
$Co_{1.3}Ti_{1.3}M$			4·4	10^8	9	2	good (0·75)
$Co_{1.5}Ti_{1.5}M$			4·2	10^8	2	1_5	very good (0·89)

$MeFe_2O_4$. A mixture of 84 wt. per cent ferrimagnetic $MeFe_2O_4$ and 16 wt. per cent non-magnetic $BaFe_2O_4$ was prepared according to the reactions XIII, XIV and XV, Table 1, by firing the samples for 2 hr at 1250°.

The $MeFe_2O_4$ crystals show an orientation of cubic [111] axes parallel to the c-axes of Me_2W in the initial mixture, i.e. the same correlation as exists in the Me_2W structure between the c-axes and one cubic [111] axis of the spinel layers (see introduction).

The presence of such a texture was concluded from X-ray diagrams obtained with X-ray beams reflected from the plane perpendicular to the c-axes of the oriented Me_2W crystals in the initial mixture. The ratio of intensities I_{hhh}/I_{hkl} of a (hhh) and a (hkl) reflection is larger than this ratio $I^\circ_{hhh}/I^\circ_{hkl}$ for non-oriented material. If

$I_{hhh}I^{\circ}_{hkl}/I_{hkl}I^{\circ}_{hhh}$ is larger than unity the above-mentioned texture is present and the orientation is the better, the larger the ratio. From the values found for this ratio it was concluded that reactions XIII and XIV gave a better oriented product than reaction XV.

The presence of such a texture was confirmed from the orientation in a magnetic field of a sample cut in the shape of a disk parallel to the [111] axes (cf. Section 2c). The NiZn-ferrite samples had uniaxial anisotropy. The $CoFe_2O_4$ sample showed two equilibrium positions making an angle of 110°.

This behaviour is expected from the well-known preferential directions of magnetization for NiZn-ferrite and $CoFe_2O_4$, which are parallel to the cubic [111] and [100] axes, respectively. For the oriented NiZn-ferrite the direction of the oriented [111] axes is thus also the preferential direction of magnetization, and the disk has an uniaxial magnetic anisotropy. In the $CoFe_2O_4$ sample, the cubic [100] directions of the oriented crystals make angles of 55° with the direction of the oriented [111] axes so that these preferential [100] directions of magnetization lie on the surface of a cone. Thus there are two preferential directions which make an angle of $2 \times 55 = 110°$ with each other in a plane that contains the axis of the cone.

4. DISCUSSION

From the fact that in, for example, reaction VI, the $Co_\delta Zn_{2-\delta}W$ crystals have the same orientation as the M crystals and that in the initial mixture only the M crystals are oriented, it is evident that the orientation of the $Co_\delta Zn_{2-\delta}W$ crystals is caused by chemical reactions that take place inside or on the M crystals. Such reactions are called topochemical reactions.[5] Since the formation of a new phase starts with nucleation, we propose the following picture. At first small $Co_\delta Zn_{2-\delta}W$ crystals (nuclei) originate inside the M crystals with the c-axes (and perhaps also the a-axes) of the two crystals parallel to each other, i.e. the M crystals act as a substrate for the epitaxial[6] growth of oriented $Co_\delta Zn_{2-\delta}W$ nuclei. The crystals present in the final product are then formed by further growth of W on these nuclei.

If a strong preference exists for nucleation of the final product on the crystals of the oriented component, which is only a fraction of the mixture, the amount of oriented material may increase considerably during a topotactical reaction. This is found for example in reaction VIII, which gives a well-oriented reaction product although the initial mixture contains only 53 wt. per cent magnetically orientable component (for $\delta = 1$). If, however, a non-oriented crystal phase of the mixture acts preferentially as a substrate for the final product, considerable amounts of a non-oriented final product are formed. This may be the case for the reactions I and XII, which give poorly oriented final products although the percentages of the magnetically orientable components (viz. 89 wt. per cent) are much higher than for reaction VIII. From these examples it is seen that the amount of oriented component in the initial mixture does not seem to be the determining factor in the orientation of the final product. This is an indication that certain crystal phases act preferentially as a substrate for the nucleation of a new phase during topotactical reactions.

Although a topotactical reaction is assumed to be initially an epitaxial process,

[5] For a definition of topochemistry see: H. REMY, *Treatise on Inorganic Chemistry* Vol. II, p. 756. Elsevier, Amsterdam (1956).
[6] For a definition of epitaxy see: A. NEUHAUS, *Fortschr. Min.* **29/30**, 129 (1950/51).

the reactions described show an essential difference from epitaxy. The final product of an epitaxial process is an intergrowth of the new phase and the substrate whereas the substrates disappear completely during the reactions described above and the final products consist of only one phase (as in reactions I–XIII). In some cases—e.g. in reaction XIII—the final product of a topotactical reaction contains two phases, but the crystal orientations in one phase (e.g. the *S* phase) bear no correlation to those in the other phase (e.g. the *B* phase), so that the epitaxial intergrowth of two crystal phases does not occur.

The term topochemistry covers the reactions described but also a great number of different phenomena. Therefore we propose the term "topotaxy" for all chemical solid state reactions that lead to a material with crystal orientations which are correlated with crystal orientations in the initial product.

The results of further investigations of topotactical reactions will be published shortly.

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CO-ORDINATION COMPOUNDS OF Ga(I)—I

CO-ORDINATION COMPOUNDS OF GALLOUS TETRACHLOROGALLATE AND GALLOUS TETRABROMOGALLATE WITH O- AND N-DONORS

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Abstract—Co-ordination compounds of gallous tetrachlorogallate, $Ga[GaCl_4]$, and gallous tetrabromogallate, $Ga[GaBr_4]$, have been prepared with several oxygen and nitrogen donor ligands of various types. Electrical conductivity, molecular weight and magnetic susceptibility measurements indicate that the complexes should be formulated as $GaL_4^+ GaX_4^-$, where L represents a monodentate ligand and X a halogen. Limited stabilization of the powerfully reducing gallous ion has been achieved. The unusual behaviour of some ligands is discussed. The stereochemistry of 4-covalent Ga(I) is discussed in the light of the results obtained.

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The problem of the structure of compounds in which gallium appears to be anomalously divalent now appears to be satisfactorily solved. The sulphide, GaS,[1] and selenide, GaSe[2] have been shown to contain trivalent gallium atoms bonded together in pairs. The dihalides, Ga_2Cl_4 and Ga_2Br_4, on the other hand, are now known from X-ray[3,4] and Raman[5,6] studies to have the ionic structures $Ga^+GaCl_4^-$ and $Ga^+ GaBr_4^-$ respectively. Monovalent gallium, the existence of which was long doubted, is known to occur in gallous sulphide, Ga_2S,[7] the monohalides, GaCl,[8] GaBr,[9] and GaI,[10] and in the compounds $GaAlCl_4$ and $GaAlBr_4$[11] which are isomorphous with gallium dichloride.

Apart from the fact that it is powerfully reducing, the chemical behaviour of the gallous ion is almost unknown. The work described here was undertaken to explore the possibility of stabilizing gallium dihalides against easy oxidation and to obtain, from their chemical properties, evidence which might help to elucidate their structures, which were unknown at the outset. Gallium dihalides were found to form co-ordination compounds with a number of ligands. These co-ordination compounds had the general empirical formula GaX_2L_2(X = Cl or Br; L = monodentate ligand), but physical measurements favoured the dimeric, ionic structure $GaL_4^+GaX_4^-$.

The investigation thus evolved into attempts to stabilize the gallous ion, which has in fact been achieved only to a limited degree by the oxygen and nitrogen donors used in this work, and to determine the stereochemistry of the complex cation. First

[1] H. Hahn and G. Frank, *Z. Anorg. Chem.* **278**, 333 (1955).
[2] K. Schubert and E. Dorre, *Naturwissenschaften* **40**, 604 (1953).
[3] G. Garton and H. M. Powell, *J. Inorg. Nucl. Chem.* **4**, 84 (1957).
[4] J. D. Corbett, H. Spencer-Palmer and H. M. Powell, Private communications concerning the isomorphism of Ga_2Cl_4 and Ga_2Br_4.
[5] L. A. Woodward, G. Garton and H. Roberts, *J. Chem. Soc.* 3723 (1956).
[6] L. A. Woodward, N. N. Greenwood, J. R. Hall and I. J. Worrell, *J. Chem. Soc.* 1505 (1958).
[7] E. Gastinger, *Z. Naturf.* **10b**, 115 (1955).
[8] E. Gastinger, *Angew. Chem.* **67**, 103 (1955).
[9] J. D. Corbett and A. Hershaft, *J. Amer. Chem. Soc.* **80**, 1530 (1958).
[10] J. D. Corbett and R. K. McMullan, *J. Amer. Chem. Soc.* **77**, 4217 (1955).
[11] J. D. Corbett, Private communication (1958).

results indicated that the gallous ion has a co-ordination number of four and later work was directed to tetradentate ligands. Ligands of different structural types have been tried and the reactivities of their complexes with gallium dihalides have been observed qualitatively. No quantitative measurements of stability constants have yet been carried out.

Although ionic compounds, gallium dihalides are appreciably soluble in benzene and other aromatic hydrocarbons. CORBETT has attributed this unusual solubility to the formation of a π-bonded complex between benzene and the gallous ion.[12] He reports that the dipole moment of Ga_2Cl_4 in benzene corresponds to an ion pair.[11] We have observed, in addition, that the fused solvates, which gallium dihalides form with benzene, are good electrical conductors, whereas the benzene solution itself is non-conducting. The inference is that the fused solvates contain complex cations of the type postulated by CORBETT. The bonding between gallous ions and benzene appears to be very weak, since the solvates readily lose benzene either to a second solvent, such as hexane, or when the pressure is reduced.

Benzene solutions of gallium dihalides are thus particularly suitable for preparing gallous complexes. The feeble co-ordination of the solvent to gallous ions is sufficient to dissolve the dihalides but it results in stronger complexes being formed with many ligands of even moderate electron donor capacity. The majority of the ionic complexes which are then formed have no affinity for benzene and are precipitated.

EXPERIMENTAL

Preparation of gallium dichloride. This was carried out by reducing gallium trichloride with gallium metal according to the method previously reported by GARTON and POWELL.[3]

Preparation of gallium dibromide. This was achieved by a similar method. Gallium dibromide cannot be purified by distillation from an excess of gallium metal or by subliming off excess tribromide, for in each case gallium dibromide disproportionates into gallium and the tribromide. GREENWOOD *et al.*[6] have reported overcoming this difficulty by repeated fractional crystallization of a melt containing Ga_2Br_4 and $GaBr_3$. A simpler procedure suffices for obtaining gallium dibromide in solution in benzene.

Gallium tribromide was reduced by heating with an excess of gallium metal *in vacuo*. The yellow liquid above excess metal had the composition $GaBr_{1\cdot8}$ and disproportionated on cooling to a mixture of gallium dibromide and gallium, with possibly some mono-bromide also present. The solid was extracted with cold benzene in which only Ga_2Br_4 is soluble. The filtered solution was used directly to prepare co-ordination compounds of gallium dibromide. Analysis showed that the Ga : Br ratio in such solution was 1 : 2. Pure Ga_2Br_4 may be precipitated from the solution as a white crystalline powder by the addition of a large excess of hexane. After washing with hexane and drying under vacuum the product had the following composition. (Found: Ga, 30·3; Br, 69·7. Calc. for Ga_2Br_4 : Ga, 30·34; Br, 69·66%).

Purification of solvents and ligands

Gallium dihalides are readily attacked by water unless the gallous ion is stabilized by co-ordination. Solutions of gallium dihalides in donor solvents such as dioxane or morpholine are decomposed only slowly by water but the solutions in benzene are very prone to attack by even traces of moisture; a brown hydrolysis product is precipitated first and, if more than a trace of water is present, the brown precipitate reduces the excess water to hydrogen and is itself converted into a mixture of gallic hydroxide and gallium metal. The affinity for water is so great that the hydrolysis product is preferentially precipitated if a ligand solution containing a trace of water is added to a benzene solution of a gallium dihalide. Pure complexes can be prepared only by scrupulously drying all solvents and ligands. A solution of gallium dichloride in benzene provided an excellent test for small amounts of

[12] R. E. RUNDLE and J. D. CORBETT, *J. Amer. Chem. Soc.* **79**, 757 (1957).

water in organic liquids and the criterion of adequate dryness in all solvents and ligands was that no brown precipitate should appear when they were added to a benzene solution of Ga_2Cl_4.

Benzene. The benzene was dried by repeated distillation from phosphorus pentoxide until the distillate failed to give a brown precipitate with a benzene solution of gallium dichloride.

Nitrobenzene. The nitrobenzene was purified by fractional distillation, followed by triple recrystallization of the fraction boiling at 207°C. After standing over phosphorus pentoxide overnight, the dry nitrobenzene was distilled under 15 mm pressure of dry nitrogen.

Dioxane. The dioxane was refluxed over Na/K alloy until a distillate was sufficiently dry by the gallium dichloride test.

Amines. All liquid amines were dried by refluxing over potassium hydroxide and distillation from fresh barium oxide. 2:2′-Dipyridyl was purified by sublimation over KOH.

Ketones and ethers. Wherever possible the ketones and ethers were dried with phosphorus pentoxide. Some, such as acetyl acetone, could not be refluxed with this drying agent and dry specimens were obtained by careful fractional distillation.

Preparation of 1:2-*ethylene morpholine*

A convenient preparation of 1,2-ethylene morpholine, not previously reported, was the following. Ethylene dibromide (40 g) and morpholine (76 g) (molar ratio 1 : 4) were refluxed together on an oil bath at 150°C for 6 hr. The white crystals of 1:2-ethylene morpholine hydrobromide which separated out were hydrolysed by 10% aqueous potash and the free ethylene morpholine was extracted with ether. The ethereal extract was evaporated to dryness and the residue recrystallized from ether. White crystals melting at 74°C were obtained in a yield of 50 g. Estimation of nitrogen by the Kjeldahl method gave the following results (Found: 14·4; calc. for $C_{10}H_{20}N_2O_2$: 14·0%).

Preparation of 2:2′:2″-*trimethoxy triethyl amine*, $N(CH_2{\cdot}CH_2{\cdot}O{\cdot}CH_3)_3$

"Technical" grade triethanolamine was converted into triethanolamine hydrochloride by the method reported by German and Knight.[13] The hydrochloride was then treated with thionyl chloride to obtain trichloro-triethylamine hydrochloride by the Mason and Gasch procedure.[14]

Trichloro-triethylamine hydrochloride (50 g) was dissolved in methanol (150 ml) and treated with a 10 per cent solution of sodium methoxide (250 ml). The mixture was refluxed on a water bath for 6 hr. Precipitated sodium chloride was filtered off and the filtrate fractionally distilled under 12 mm pressure. 2:2′:2″-Trimethoxy triethylamine distilled over at 107°C. The amine was dried over anhydrous sodium sulphate and redistilled under 12 mm pressure. A nitrogen estimation yielded the following results (Found: 7·14; calc. 7·33%).

2:2′-*Dimethoxy diethyl ether.* This preparation was carried out by the reaction between 2:2′-dichloro diethyl ether and sodium methoxide in methanol according to the method described by Cretcher and Pettenger.[15]

Preparation of co-ordination compounds

The method of preparation was essentially the same in nearly all cases. A benzene solution of a slight excess of the ligand was allowed to react with gallium dihalide in benzene and the insoluble complex filtered off. The apparatus is illustrated in Fig. 1.

The glassware was dried at 200°C and kept in a vacuum desiccator until ready to be assembled. The assembled apparatus was evacuated and filled with dry nitrogen. A known volume of a standard gallium dihalide solution was siphoned into the reaction vessel *A*. The required volume of ligand solution was run into *A* from the dropping funnel *B*, with rapid stirring. By opening the wide-bore stopcock *E*, the slurry of complex and benzene was run on to a sintered glass filter disk in the tube

[13] F. E. E. German and O. S. Knight, *J. Amer. Chem. Soc.* **55**, 4150 (1933).
[14] J. P. Mason and D. J. Gasch, *J. Amer. Chem. Soc.* **60**, 2816 (1938).
[15] L. H. Cretcher and W. H. Pettinger, *J. Amer. Chem. Soc.* **47**, 163 (1925).

F and filtered by reducing the pressure at *G*. Benzene for washing was introduced via the dropping funnel *C* and then the precipitate was partially dried by passing a rapid stream of dry nitrogen through it from the side tube *H*. Tube *F* was detached and capped with ground-glass stoppers for transfer to a vacuum desiccator where it was dried overnight under high vacuum. Subsequent handling of the complexes was done in a dry box, so far as possible.

Analytical methods

For estimation of gallium and halogen, about 0·1 g of the complex was dissolved in 25 ml of dilute sulphuric acid. Hydrogen was evolved and when the effervescence had subsided the solution was boiled gently for a few minutes to complete the oxidation of gallous to gallic.

Gallium was determined volumetrically by the method of DOLEŽAL *et al.*,[16] in which gallium is

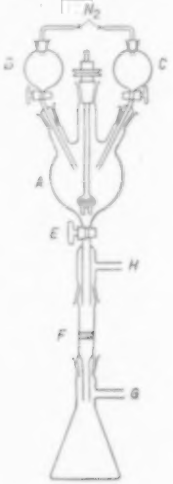


FIG. 1.

titrated against a standard solution of the disodium salt of ethylene diamine tetra-acetic acid, with morin as an ultra-violet fluorescent indicator.

Chlorine and bromine were also estimated volumetrically by a small scale adaptation of VOLHARD's method. Nitrobenzene was added to avoid filtering off the precipitated silver halides.

Nitrogen analyses were performed by the standard micro-Kjeldahl method.

Physical measurements

Magnetic measurements. These were performed on samples of about 50 mg average weight contained in small gelatin pill-capsules to exclude air. Measurements were made at several different field strengths at room temperature. The Faraday-type susceptibility balance which was employed had a beryllium–copper helical spring combined with a cathetometer to measure the force on the specimen. Weight changes were measured to within 0·005 mg.

Electrical conductivity measurements. The measurements of electrical conductivity were made in nitrobenzene solutions, in the concentration range 10^{-2}–10^{-4} M, with a diptype cell having platinized platinum electrodes. Molar conductivities are recorded for a concentration of 10^{-3} M in each case.

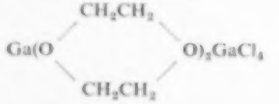
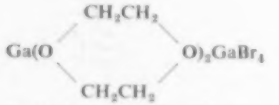
Molecular weight. The determinations of molecular weight were carried out cryoscopically by the Beckmann method. Nitrogen was passed continuously into the apparatus and allowed to escape from a closely fitting stirrer gland to prevent ingress of moisture.

RESULTS

In view of the number of complexes which were prepared, a separate description of each will not be given. Table 1 lists the compositions and general properties of co-ordination compounds formed by some O- and N-donors with gallium dichloride and

[16] J. DOLEŽAL, V. PATROVSKÝ, Z. ŠULCEK and J. ŠVASTA, *Chem. Listy* **40**, 1517 (1955).

Table 1

Compound	Analytical results: Gallium found	Gallium calc.	Chlorine found	Chlorine calc.	Bromine found	Bromine calc.	Nitrogen found	Nitrogen calc.	Melting pt. or decomp. pt.	Reactions: Air	Water	Dil. acids	Dil. alkalis
$Ga(C_6H_5OMe)_4GaCl_4$	19·0	19·5	19·8	19·9					decomposes above 130°C	*A*	*A*	*F*	*F*
$Ga(C_6H_5OMe)_4GaBr_4$	16·2	15·6			35·9	35·9			decomposes above 130°C	*A*	*A*	*F*	*F*
	30·4	30·5	30·1	31·0					48°C with decomp.	*A*	*A*	*F*	*F*
	22·0	22·0			49·6	50·3			71°C with decomp.	*A*	*A*	*F*	*F*
$Ga[(MeOC_2H_4)_2O]_2GaCl_4$	24·7	25·4	27·2	25·8					146°C with decomp.	*A*	*A*	*F*	*F*
$Ga[(MeOC_2H_4)_2O]_2GaBr_4$	19·2	19·2			44·2	44·0			127°C with decomp.	*A*	*A*	*F*	*F*
$Ga(Hacac)_2GaCl_4$ (*a*)	29·1	29·0	30·8	29·5					140°C with decomp.	*B*	*B*	*F*	*F*
$Ga(Hacac)_2GaBr_4$ (*a*)	21·0	21·2			47·0	48·5			138°C with decomp.	*B*	*B*	*F*	*F*
$Ga(Hbzac)_2GaCl_4$ (*b*)	22·9	23·0	23·5	23·4					124°C with decomp.	*B*	*B*	*F*	*F*
$Ga(Hbzac)_2GaBr_4$ (*b*)	17·8	17·8			41·0	40·8			101°C with decomp.	*B*	*B*	*F*	*F*
$Ga(salald)_2GaCl_4$ (*c*)	26·4	26·5	26·9	27·0					decomposes above 140°C	*A*	*A*	*F*	*F*
$Ga(salald)_2GaBr_4$ (*c*)	19·9	19·8			45·8	45·5			decomposes above 140°C	*A*	*A*	*F*	*F*
$Ga(Et_2NH)_4GaCl_4 2C_6H_6$	18·7	18·9	19·3	19·2			7·8	7·6	decomposes above 120°C	*A*	*A*	*F*	*F*
$Ga(en)_2GaCl_4 2C_6H_6$ (*d*)	25·6	25·6	26·1	26·0			10·0	10·2	decomposes above 120°C	*A*	*A*	*F*	*F*
$Ga(en)_2GaBr_4 2C_6H_6$ (*d*)	19·4	19·3			44·5	44·3	7·7	7·8	decomposes above 120°C	*A*	*A*	*F*	*F*
$Ga(C_6H_5NH_2)_4GaCl_4 2C_6H_6$	17·0	17·2	17·7	17·5			6·3	6·9	decomposes above 120°C	*A*	*A*	*F*	*F*
$Ga(C_6H_5NH_2)_4GaBr_4 2C_6H_6$	14·0	14·1			32·4	32·4	5·7	5·7	decomposes above 120°C	*A*	*A*	*F*	*F*
$Ga(opd)_2GaCl_4C_6H_6$ (*e*)	24·3	24·2	24·7	24·6			9·9	9·8	decomposes above 120°C	*A*	*A*	*F*	*F*
$Ga(dipy)_2GaCl_4$ (*f*)	23·3	23·5	23·9	23·9					decomposes above 120°C	*C*	*C*	*F*	*F*
$Ga(dipy)_2GaBr_4$ (*f*)	18·0	18·1			41·2	41·4			decomposes above 120°C	*C*	*C*	*F*	*F*
$Ga(salox)_2GaCl_4$ (*g*)	25·2	25·1	25·6	25·5					62°C with decomp.	*A*	*A*	*F*	*F*

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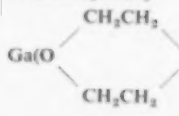
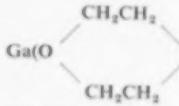
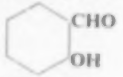
$Ga(salox)_2GaBr_4$	(*g*)	19·0	19·0			43·8	43·6		decomposes above 110°C	*A*	*A*	*F*	*F*
		30·6	30·6	31·1	31·1				149°C with decomp.	*D*	*E*	*F*	*F*
		22·2	22·0			50·0	50·5		198°C with decomp.	*D*	*E*	*F*	*F*
$Ga(etmorph)GaCl_4$	(*h*)	28·9	29·0	29·4	29·5				81°C with decomp.	*D*	*E*	*F*	*F*
$Ga(etmorph)GaBr_6$	(*h*)	21·2	21·2			48·5	48·5		decomposes over 175°C	*D*	*E*	*F*	*F*
$Ga(tmten)GaCl_4$	(*i*)	29·4	29·6	30·0	30·0				not observed	*D*	*E*	*F*	*F*
$Ga(dith)_2GaCl_4$	(*j*)	17·5	17·5	17·9	17·9				not observed	*D*	*D*	*F*	*G*

(*a*) Hacac = acetylacetone, $CH_3{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CH_3$

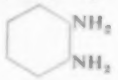
(*b*) Hbzac = benzoylacetone, $C_6H_5{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CH_3$

(*c*) Salald = salicylaldehyde,



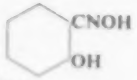
(*d*) en = ethylene diamine, $H_2N{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$

(*e*) opd = *o*-phenylene diamine

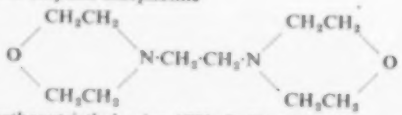


(*f*) dipy = dipyridyl

(*g*) salox = salicylaldoxime



(*h*) etmorph = 1:2-ethylene morpholine



(*i*) tmten = trimethoxytriethylamine $(CH_3{\cdot}O{\cdot}CH_2CH_2)_3N$

(*j*) dith = "dithizone," i.e. diphenylthiocarbazone $C_6H_5{\cdot}N{:}N{\cdot}CS{\cdot}NH{\cdot}NH{\cdot}C_6H_5$

A = Readily decomposed and oxidized
B = Slowly decomposed and oxidized
C = Rapidly decomposed and oxidized
D = Stable
E = Decomposed by hot water
F = Soluble with evolution of hydrogen
G = Moderately stable

gallium dibromide. With the exception of the 2:2′-dipyridyl and dithizone complexes, which were red, all the compounds listed were white or faintly cream coloured. All decomposed on heating, some without melting; others melted with decomposition. All were decomposed on dissolution in water, but, unlike gallium dihalides and their solutions in aromatic hydrocarbons, the primary action of water was not to produce a

Table 2.—Molar conductivities at 10^{-3} M and apparent molecular weights of gallous complexes in nitrobenzene

Compound	Mol. cond. (mhos)	Apparent mol. wt. at approx. M/100	
		Observed	Calc. assuming complete dissociation into two ions
$Ga_2Cl_4(diox)_2$	22·0		
$Ga_2Br_4(diox)_2$	19·6		
$Ga_2Cl_4(Hacac)_2$	22·5	280	241
$Ga_2Br_4(Hacac)_2$	20·6	400	330
$Ga_2Cl_4(Hbzac)_2$	21·4	355	303
$Ga_2Br_4(Hbzac)_2$	20·6		
$Ga_2Cl_4(salald)_2$	20·4		
$Ga_2Br_4(salald)_2$	19·7		
$Ga_2Cl_4(dipy)_2$	21·2		
$Ga_2Cl_4(dipy)_2$	19·9		
$Ga_2Cl_4(dithizone)_2$	17·5		

brown hydrolysis product. A further point of difference was that the gallous complexes were converted entirely into gallic compounds in aqueous solution; gallium dihalides and their benzene solution always yield some gallium metal by disproportionation.

Gallium dihalides react violently with nitrobenzene to give tarry products or, with a large excess of nitrobenzene, brownish-black solutions. The solutions are conducting and the molar conductivities, based on $Ga^+GaX_4^-$, are in the range 15–20 mhos at about 10^{-3} M, but rather erratic. It is probable, therefore, that gallium dihalides behave as 1 : 1 electrolytes in nitrobenzene but owing to reaction with the solvent the results are unreliable. Gallous complexes did not react with dry nitrobenzene. Although the gallous ion has not been stabilized against oxidation by water, it appears to have been stabilized against oxidation by nitrobenzene.

The results of electrical conductivity and molecular weight measurements in nitrobenzene are summarized in Table 2. Molar conductivities of the gallous complexes at 10^{-3} M are comparable with the molar conductivities of other 1 : 1 electrolytes in nitrobenzene (see, e.g., Foss and Gibson;[17] Kabesh and Nyholm[18]), in accord with the ionic structure $GaL_4^+GaX_4^-$. Molecular weights in the same solvent are also in accord with this structure and indicate a high degree of dissociation.

A molecular weight determination in a non-ionizing solvent was considered

[17] M. E. Foss and C. S. Gibson, *J. Chem. Soc.* 3063 (1949).
[18] A. Kabesh and R. S. Nyholm, *J. Chem. Soc.* 38 (1951).

desirable. Accordingly, the molecular weights of the two dioxane complexes were measured in dioxane, with the following results.

Compound	Calculated mol. wt.	Observed mol. wt. in dioxane
$Ga(Diox)_2GaCl_4$	457	495
$Ga(Diox)_2GaBr_4$	635	650

No suitable non-co-ordinating, non-ionizing solvent could be found for the other complexes but it is likely that the similarity in all their other properties is continued in the formation of ion pairs in non-dissociating solvents.

TABLE 3.—GRAM AND MOLAR MAGNETIC SUSCEPTIBILITIES OF GALLOUS COMPLEXES TOGETHER WITH GRAM-ION SUSCEPTIBILITY OF Ga^+

Compound	$\chi_g \times 10^6$	$\chi_m \times 10^6$	$\chi_{Ga} \times 10^6$
$Ga_2Cl_4(anisole)_4$	−0·581	−414	−12
$Ga_2Br_4(anisole)_4$	−0·509	−453	−11
$Ga_2Cl_4(diox)_2$	−0·527	−241	−12
$Ga_2Br_4(diox)_2$	−0·441	−280	−11
$Ga_2Cl_4(dimet)_2$	−0·548	−301	−12
$Ga_2Br_4(dimet)_2$	−0·470	−342	−13
$Ga_2Cl_4(Hacac)_2$	−0·483	−232	− 9
$Ga_2Br_4(Hacac)_2$	−0·419	−276	−13
$Ga_2Cl_4(Hbzac)_2$	−0·477	−289	−12
$Ga_2Br_4(Hbzac)_2$	−0·422	−331	−14
$Ga_2Cl_4(salald)_2$	−0·467	−245	−11
$Ga_2Br_4(salald)_2$	−0·404	−284	−10
$Ga_2Cl_4(dipy)_2$	−0·534	−317	−12
$Ga_2Br_4(dipy)_2$	−0·462	−356	−11
$Ga_2Cl_4(salox)_2$	−0·482	−268	−13
$Ga_2Br_4(salox)_2$	−0·418	−307	−12
$Ga_2Cl_4(etmorph)$	−0·514	−248	−11
$Ga_2Br_4(etmorph)$	−0·437	−288	−11
$Ga_2Cl_4(morph)_2$	−0·528	−240	−12
$Ga_2Br_4(morph)_2$	−0·440	−278	−10

Table 3 gives the results of magnetic susceptibility measurements on gallous complexes. They are all diamagnetic and the possibility of divalent gallium is thus ruled out. The gram-ion susceptibility of Ga^+ was determined by the additive rule of molar susceptibilities. Published values of the molar susceptibilities of Ga(III), Cl^- and Br^-[19] were used, together with published susceptibilities of the ligands, if available, otherwise the magnetic susceptibilities of the ligands were also measured. No bond corrections were applied. Reasonably constant values for the gram-ion

[19] P. W. SELWOOD, *Magnetochemistry*. Interscience Publishers, New York (1956).

susceptibility of Ga^+ were obtained, the average being -12×10^{-6} c.g.s. units. This compares with a value of -14×10^{-6} c.g.s. units calculated in a similar way from Klemm's[20] measurement of the susceptibility of gallium dichloride.

DISCUSSION

It is clear that gallium dichloride and dibromide readily form co-ordination compounds with a variety of O- and N-donor ligands. The complexes have empirical formulae of the type GaX_2L_2, except for a few which also contain varying stoicheiometric amounts of benzene, probably as solvent of crystallization. Magnetic susceptibility measurements have demonstrated that there is no unpaired electron in these complexes and the monomeric formula is ruled out for the solids. Electrical conductivity measurements in nitrobenzene suggest that the complexes are binary electrolytes and molecular weight measurements in the same solvent are in accord with a dimer dissociated into two ions. Finally, the molecular weights of the dioxane complexes measured in dioxane correspond to the dimeric formula. Structures of gallium dihalides are now established as $Ga^+GaX_4^-$. Co-ordination compounds of gallium dihalides, therefore, probably have structures of the type $(GaL_4)^+(GaX_4)^-$, in which the gallous ion has a co-ordination number of four.

In the proposed structure, Ga(I) atoms have a decet of valency electrons and the question of the stereochemistry of the 4-co-ordinated gallous ion immediately arises. Some 4-co-ordinated complexes of Tl(I) and Pb(II) are stated to have a planar structure but the X-ray studies on which this assertion is based are incomplete.[21] There is, unfortunately, no complete structural investigation of any 4-covalent complex of In(I), Tl(I), Sn(II) or Pb(II) from which the probable stereochemistry of the gallous ion might be deduced. Pb(II), for example, commonly occurs either as the free ion or covalently linked to two atoms only. However, PbO and SnO do not have the usual ionic structures but crystallize in a rather peculiar arrangement of four oxygen neighbours all lying to one side of a Pb or Sn atom. If the metal–oxygen bonds are covalent in character, the metals must have a decet of valency electrons and there is a formal analogy with 4-co-ordinated Ga(I) and Tl(I).

Tl(I) halides crystallize in ionic structures but InBr has a similar structure to those of PbO and SnO, that is with four bromine atoms lying in a plane and equidistant from an indium atom which is itself displaced from the plane.[22] It is probable that the 4-co-ordinated complexes of all these metals with a decet of valency electrons have related structures which can be achieved with little distortion by placing the co-ordinating groups at four of the five apices of a trigonal bipyramid.[23]

The *s* pair of electrons is not therefore stereochemically inert, which would be the case if the 4-co-ordinated complexes of Tl(I) and Pb(II) were, in fact, planar and thus presumably making use of p^2d^2 hybrid orbitals of the metal atoms. The trigonal bipyramid requires the hybrid orbitals sp^3d; in this case the lone pair is not stereochemically inert but occupies one apex of the trigonal bipyramid.

The evidence cited for the planar co-ordination of Pb(II) and Tl(I) is insufficient to distinguish between (a) a planar arrangement of the metal and four donor atoms and (b) the arrangement derived from the trigonal bipyramid which places the metal

[20] W. Klemm and W. Tilk, *Z. Anorg. Chem.* **207**, 161 (1932).
[21] E. G. Cox, A. J. Shorter and W. Wardlaw, *J. Chem. Soc.* 1886 (1938); *Nature, Lond.* **139**, 71 (1937).
[22] N. C. Stephenson and D. P. Miller, *Austr. J. Sci. Res.* A **3**, 581 (1950).
[23] R. J. Gillespie and R. S. Nyholm, *Quart. Rev.* **11**, 339 (1957).

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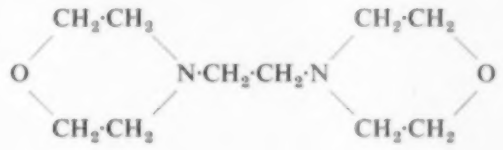
atom outside the plane of the donor atoms. It is adequate to rule out the remote possibility of a tetrahedral configuration for those particular complexes.

Structures of the gallous complexes described above cannot in general be deduced from the available experimental evidence. The majority of ligands which were used were mono- or bi-dentate and sufficiently small to fit almost any arrangement of four bonds from the gallous ion. Two ligands were specifically synthesized to assist the structural investigation.

The first, 1:2-ethylene morpholine,



is quadridentate and if it uses all four of its potential donor atoms to co-ordinate to one gallous ion, can only form a planar grouping around the gallous ion, or, by a slight twist to the molecule, will allow the gallous ion to be displaced from the plane of the O and N atoms [Fig. 2(II)]. If the configuration of the bonds from Ga(I) is planar or in the form of the flat pyramid derived from a trigonal bipyramid, 1:2-ethylene morpholine should form stable complexes with gallium dihalides of the type $[Ga(\text{ethylene morpholine})]^+[GaX_4]^-$. Complexes of this formula have been prepared from both Ga_2Cl_4 and Ga_2Br_4. Compared to the other complexes which have been described, the ethylene morpholine compounds were quite inert. They could not be characterized further owing to their insolubility.

The second ligand which requires a definite arrangement of four bonds from the gallous ion was 2:2′:2″-trimethoxytriethylamine ($N(CH_2{\cdot}CH_2{\cdot}O{\cdot}CH_3)_3$) (tmten). If all donor atoms co-ordinate to the same gallous ion, a tetrahedral bond configuration is preferred. Accordingly, it was not expected that this ligand would form a stable complex of the composition [Ga(tmten)] $[GaX_4]$. However, a moderately stable complex of that formula was obtained but, like the ethylene morpholine complex, it was insoluble in all the solvents tried and it is impossible to say definitely that a discrete ion $[Ga(\text{tmten})]^+$ is formed. The alternatives are some form of polymerized complex where the trimethoxytriethylamine molecule is shared among more than one 4-covalent gallous ion, which the shape of the ligand makes unlikely, or discrete ions where the ligand does not co-ordinate with all four donor atoms. Since the co-ordination number of Ga(I) in its stable complexes has not so far been less than four, the second alternative has no precedent to recommend it.

Assuming, in the absence of molecular weight and conductivity data, that discrete ions are formed, we are forced to the conclusion that Ga(I) can form four covalent bonds in two entirely different configurations. If the *s* pair of electrons is really inert, the formation of both planar and tetrahedral bonds requires the use of two different and unusual sets of hybrid orbitals. If, on the other hand, we assume that, in common with other non-transition elements having a decet of valency electrons, Ga(I) forms the set of hybrid orbitals sp^3d directed to the corners of a trigonal bipyramid, then the formation of stable complexes with two such sterically dissimilar ligands as 1:2-ethylene morpholine and 2:2′:2″-trimethoxytriethylamine is explicable.

Fig. 2(I) shows the arrangement of bonds from a gallous ion in a complex $(GaL_4)^+$, with the lone pair of electrons occupying the position where there is minimum electrostatic repulsion between it and the four bond pairs. Repulsion between lone pair and bond pair is greater than that between bond pair and bond pair with the result that the Ga–L bonds nearest to the lone pair are pushed away from the lone pair and the four L groups approach a planar configuration to one side of the gallous ion. Mono- and bi-dentate ligands have no difficulty in adopting this arrangement and 1:2-ethylene morpholine will also conform [Fig. 2(II)].

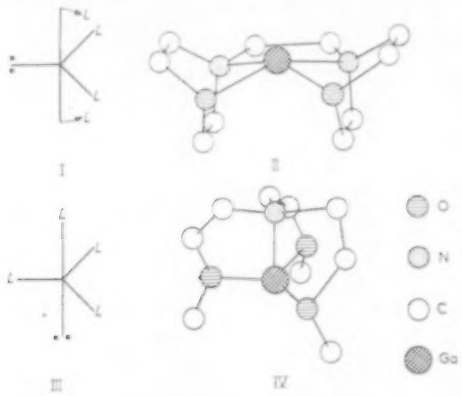


Fig. 2.

The lone pair may also reside at a different apex of the trigonal bipyramid as shown in Fig. 2(III), where the four L groups are now in the form of a tetrahedron like the donor atoms of trimethoxytriethylamine [Fig . 2(IV)]. This location of the lone pair increases the electrostatic repulsion energy but this unfavourable circumstance is likely to be considerably outweighed by the large entropy effect attending the formation of a trimethoxytriethylamine complex.

Further work to establish the stereochemistry of 4-co-ordinated Ga(I) is now in progress. In particular, an X-ray investigation of (bis-1:4-dioxane) gallous tetrachlorogallate, $Ga(diox)_2^+GaCl_4^-$, has begun and the results will be presented in a later communication. It would be desirable to establish the stereochemical behaviour of all the IIIB and IVB sub-group metals in their lower valency states to confirm or deny the unusual stereochemical inertness of a pair of valency electrons which has been postulated for Tl and Pb.

There are some other unusual results to be considered. The complexes usually formed by β-diketones, salicylaldehyde and salicylaldoxime involve replacement of enolic or phenolic hydrogen atoms. Complexes of these ligands with Ga(I) apparently do not form with elimination of hydrogen. This difference in behaviour probably arises from the fact that strictly anhydrous and neutral conditions were employed in the precipitation of the gallous complexes, whereas alkaline conditions are commonly employed to prepare complexes of, for example, the acetylacetonate type. Taking as an example the acetyl acetone complex of Ga_2Cl_4, one might argue that the structure could be $2H^+Ga(acac)_2^-GaCl_4^-$. Electrical conductivity and molecular weight measurements in nitrobenzene are wholly against such a formulation. In any case, it is doubtful if hydrogen ions can exist in the presence of Ga(I) for reduction of

hydrogen ions to hydrogen takes place readily even in anhydrous dioxane or benzene. It appears that β-diketones, salicylaldehyde and salicylaldoxime behave as straightforward bidentate donors with Ga(I) under these particular conditions.

Complexes with pyridine and 2:2′-dipyridyl were rather unstable, the former so much so that they have not been fully characterized. Dipyridyl complexes were unusual also in their deep red colour. The instability and the colour may be due to the affinity of the aromatic ring for electrons and its easy reduction. Undiluted pyridine reacts vigorously with gallium dihalides, evolving hydrogen and being converted into condensed products. This behaviour may be compared with that of the alkali metals which form coloured solutions in pyridine and yield polypyridyls.

The inclusion of dithizone among the oxygen and nitrogen donors is justified by the fact that, in this case, it is not certain which of the potential donor atoms are co-ordinated to the gallous ions. The sulphur atom may contribute to the markedly greater stability of the dithizone complexes contrasted with most of the others considered here. Dithizone complexes of gallium dihalides are moderately soluble in benzene and chloroform to give deep red solutions. They are stable in water and will even resist dilute aqueous alkali for some time. It is impossible to say, at present, if it is the sulphur atom which is co-ordinated to the gallous ion and conferring on it this greater resistance to oxidation.

Acknowledgements—We wish to thank Imperial Chemical Industries Ltd. for a grant towards the purchase of gallium metal. S. M. A. wishes to thank the Government of Pakistan for a maintenance award and G. G. to thank Oxford University for an I.C.I. Research Fellowship during the tenures of which this work was carried out.

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THE THERMAL DECOMPOSITION OF THE HEAVIER RARE EARTH METAL CHLORIDE HYDRATES

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Abstract—The thermal decomposition of the 6-hydrates of europium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium chlorides was studied on the thermobalance. The 6-hydrates began to lose water of hydration in the 65° to 95°C temperature range. Because of the decreasing basicity of the metal ions, horizontal weight levels corresponding to the anhydrous metal chlorides were not found. Instead, the decomposition curves in the 200° to 265°C temperature range corresponded to the composition, $MOCl{\cdot}2MCl_3$. On increasing the temperature, these compounds decomposed to form the metal oxychlorides in the 360° to 425°C temperature range.

THE thermal decomposition of the yttrium, scandium, and lighter rare earth metal chloride hydrates has previously been discussed.[1] It was found that the pyrolysis, in air, followed the general pattern: $MCl_3{\cdot}6H_2O \rightarrow MCl_3{\cdot}nH_2O \rightarrow MCl_3 \rightarrow MOCl$. The more basic metal chloride hydrates decomposed to form weight levels of almost pure anhydrous chloride; while as the basicity of the metal ions decreased, the MCl_3 levels contained increasingly larger amounts of oxychloride content. However, along with decreasing basicity, the tendency to form intermediate metal chloride hydrates, $MCl_3{\cdot}nH_2O$, increased. It was evident that the less basic ions, which are also smaller in radii, formed the more stable intermediate hydrates.

The terminal decomposition product, except in the case of scandium and cerium (III), was the metal oxychloride. It was found that the minimum oxychloride level temperatures decreased in the order:

$$La > Pr > Nd > Sm > Y > Gd.$$

With scandium and cerium, the terminal products were the oxides, Sc_2O_3 and CeO_2, respectively.

To complete the study of this series, this investigation is concerned with the thermal decomposition of the heavier rare earth metal chloride hydrates—those from europium (excluding gadolinium) to lutetium. It was of interest to extend the trends revealed in the thermal decomposition patterns of the lighter rare earths to those of the heavier rare earth chlorides.

EXPERIMENTAL

Thermobalance. An automatic recording thermobalance as previously described was used.[2] Sample sizes ranged from 90 to 100 mg with a linear heating rate of 5·4°C per min. A slow stream of air was passed through the furnace during the pyrolysis. Samples were run in duplicate or triplicate.

Chemicals. The rare earths were obtained as the oxides of 99·9 per cent purity from the St. Eloi Chemical Corp., Newtown, Ohio, and the Lindsay Chemical Co., West Chicago, Ill.

[1] W. W. WENDLANDT, *J. Inorg. Nucl. Chem.* **5**, 118 (1957).
[2] W. W. WENDLANDT, *Analyt. Chem.* **30**, 56 (1958).

Preparation of the rare earth chloride hydrates. The same general procedure as previously described was used.[1]

DISCUSSION

The thermal decomposition curves for the heavier rare earth metal chloride hydrates are given in Figs. 1 and 2. The composition data is given in Table 1.

TABLE 1.—THE THERMAL DECOMPOSITION OF THE RARE EARTH CHLORIDE HYDRATES—WEIGHT LOSS DATA

Rare earth chloride 6-hydrate	Weight loss (%) MCl_3 Theor.	MCl_3 Found	$MOCl{\cdot}2MCl_3$ Theor.	$MOCl{\cdot}2MCl_3$ Found	MOCl Theor.	MOCl Found	Other Theor.	Other Found
Europium			34·49	33·4	44·48	44·7	26·76	27·5(165°)
				33·0		44·1		26·8
								as $EuCl_3{\cdot}O{\cdot}5H_2O$
Terbium			33·85	33·8(250°)		43·3		
				34·6	43·66	44·2		
Dysprosium			32·89	33·3(235°)		42·8		
				32·9	43·24	42·4		
Holmium	28·49	28·3(175°)		33·7(220°)		42·6		
		28·0	33·32	33·9	42·97	42·4		
Erbium			33·12	32·5(220°)		42·4		
				33·2	42·70	42·6		
Thulium	28·20	29·1(185°)		33·5(225°)		42·8		
		29·1	32·97	32·9	42·51	42·8		
Ytterbium			32·62	31·7(205°)		41·4		
				32·4	42·07	41·7		
Lutetium			32·46	32·9(200°)		42·7		
				31·5	41·86	41·9		

Europium (*Fig.* 1D). The initial compound began to lose absorbed water at a little above room temperature. After the loss of this water, a horizontal weight level was observed from 50° to 80°C which corresponded to the formula, $EuCl_3{\cdot}6H_2O$. The 6-hydrate began to evolve water of hydration at 80°C, giving a break in the curve at 165°C which corresponded approximately to the composition, $EuCl_3{\cdot}0{\cdot}5H_2O$. Further weight loss then took place to give another horizontal weight level, from 225° to 265°C, which corresponded roughly to a mixed metal oxychloride–chloride, $EuOCl{\cdot}2EuCl_3$. Above 265°C, further decomposition ensued, resulting in the EuOCl level at 380°C.

It is interesting to note that an anhydrous metal chloride level was not obtained; instead, the composition approached that of the 0·5-hydrate. The existence of a mixed metal oxychloride–chloride was also observed, the presence of which is also indicated in the other heavier rare earth chlorides.

Terbium (*Fig.* 2B). The hydrate, $TbCl_3{\cdot}6H_2O$, began to evolve water of hydration at 65°C. After a break in the curve at 200°C, a horizontal weight level was observed from 250° to 300°C. The composition of the curve in this region corresponded

approximately to the formula, $TbOCl{\cdot}2TbCl_3$. Above 300°C, further decomposition took place to give the TbOCl level at 425°C. At elevated temperatures, namely 715°C, the oxychloride began to decompose to form the oxide, Tb_4O_7. However, since the thermobalance has an upper furnace temperature limit of ~850°C, the conversion, $TbOCl \rightarrow Tb_4O_7$, was not completed.

Dysprosium (*Fig.* 2D) The hydrate, $DyCl_3{\cdot}6H_2O$, began to evolve water of hydration at 90°C. Breaks were observed in the curve at two points, 190° and 235°C.

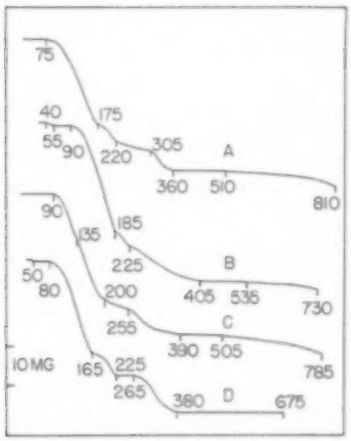

FIG. 1.—Thermograms of the rare earth metal chloride 6-hydrates.
A. Holmium B. Thulium
C. Lutetium D. Europium

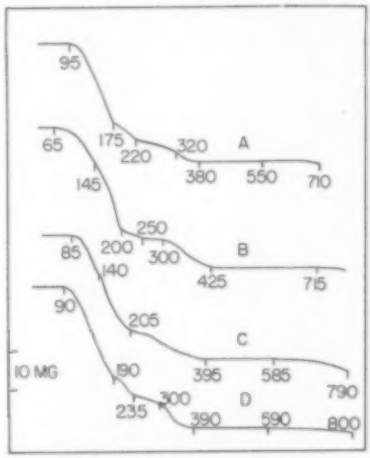

FIG. 2.—Thermograms of the rare earth metal chloride 6-hydrates.
A. Erbium B. Terbium
C. Ytterbium D. Dysprosium

The composition of the curve at the 190°C break is not known but at the 235°C break, it corresponded approximately to the formula, $DyOCl{\cdot}2DyCl_3$. No horizontal weight level was observed but instead, a gradual weight loss took place. This weight loss became more rapid above 300°C, resulting in the DyOCl level at 390°C. Decomposition to the oxide, Dy_2O_3, began to take place above 590°C, however, as in the case of terbium, the process was not completed in the temperature range employed.

Holmium (*Fig.* 1A). The hydrate, $HoCl_3{\cdot}6H_2O$, began to evolve water of hydration at 75°C. Two breaks were observed in the curve, one at 175°C, the other at 220°C. The composition of the curve at the 175°C break corresponded approximately to the formula, $HoCl_3$. At the 220°C curve break, the composition approached the formula, $HoOCl{\cdot}2HoCl_3$. A gradual weight loss then took place above 220°C, followed by a more rapid weight loss above 305°C, resulting in the HoOCl level at 360°C. Decomposition to the oxide, Ho_2O_3, began to take place above 510°C.

Erbium (*Fig.* 2A). The hydrate, $ErCl_3{\cdot}6H_2O$, was the most stable of all of the compounds studied. Water of hydration began to come off at 95°C, giving breaks in the curve at 175° and 220°C. The composition of the curve at the 175°C break is unknown, but presumably, it is the anhydrous chloride. The 220°C curve break corresponded approximately to the composition, $ErOCl{\cdot}2ErCl_3$. After further weight loss, the ErOCl level was obtained at 380°C. The decomposition to the oxide, Er_2O_3, began to take place above 550°C. It is worthy to note that the erbium curve is remarkably similar to the holimum curve.

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Thulium (*Fig.* 1B). The initial compound began to lose absorbed water at about 40°C. This was followed by a horizontal weight level, from 55° to 90°C, which corresponded to the composition, $TmCl_3 \cdot 6H_2O$. Above 90°C, the 6-hydrate began to evolve water of hydration, giving breaks in the curve at 185° and 225°C. The curve compositions for these breaks approximated the formulae, $TmCl_3$ and $TmOCl \cdot 2TmCl_3$, respectively. Further weight loss above 225°C resulted in the TmOCl level at 405°C. The decomposition to the oxide, Tm_2O_3, began at 535°C.

Ytterbium (*Fig.* 2C). The hydrate, $YbCl_3 \cdot 6H_2O$, began to evolve water of hydration at 90°C. Two intermediate breaks were then observed in the curve, one at 145°C, the other at 205°C. The composition of the curve at the 145°C break is unknown, but at the 205°C break, the composition corresponded approximately to the formula, $YbOCl \cdot 2YbCl_3$. Further weight loss took place above 205°C, resulting in the YbOCl level at 395°C. The decomposition to the oxide, Yb_2O_3, began to take place above 585°C.

Lutetium (*Fig.* 1C). The hydrate, $LuCl_3 \cdot 6H_2O$, began to evolve water of hydration at 90°C. Two intermediate breaks were then observed in the curve, one at 135°C, the other at 200°C. The thermogram pattern and the decomposition temperatures closely paralleled the ytterbium curve. The composition of the curve at the 135°C break is unknown, but at the 200°C break, the composition corresponded approximately to the formula, $LuOCl \cdot 2LuCl_3$. After further weight loss above 200°C, the LuOCl level began at 390°C. The decomposition to the oxide, Lu_2O_3, began at 505°C. It should be noted that lutetium possessed the shortest oxychloride level of all of the rare earths studied.

General observations. The thermal decomposition patterns for the heavier rare earth chloride hydrates are those that would be expected for the transition to decreasing basicity and decreasing ionic radii of the metal ions. There was little evidence for the formation of weight levels for stable intermediate hydrates or for the anhydrous metal chlorides. Evidence was observed for the formation of compounds intermediate between the metal chloride and the oxychloride. These compounds were of the general formula, $MOCl \cdot 2MCl_3$. Horizontal weight levels were found, in all cases, for the metal oxychloride. However, as the temperature was increased, it was found that the oxychlorides began to decompose to form the metal oxides. Unfortunately, the upper limit of the thermobalance furnace did not permit the attainment of the pure metal oxide weight levels.

Acknowledgement—It is a pleasure to acknowledge RICHARD MANDLE of the Davison Chemical Co., and the Lindsay Chemical Co., for the samples of the thulium and lutetium oxides.

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THERMOGRAVIMETRIC PYROLYSIS OF SOME 1:2:3-BENZOTRIAZOLE COMPOUNDS OF OSMIUM

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Abstract—This paper arises from a general study of the interaction of the platinum metals with 1:2:3-benzotriazole. The thermogravimetric pyrolysis of several 1:2:3-benzotriazole co-ordination compounds of certain metals and of certain halides of osmium have been determined using a thermobalance. It was found that all of the compounds were stable up to at least 110°C and that decomposition of the compounds occurred between 380° and 560°C. The co-ordination compounds that were hydrated lost their water of hydration in the temperature range 130°–150°C. Thermogravimetric analyses of the co-ordination compounds gave support to the proposed formulas of the 1:2:3-benzotriazole compounds of osmium.

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DURING the course of study of the interaction of 1:2:3-benzotriazole with osmium, thermogravimetric pyrolyses of several co-ordination compounds of osmium with 1:2:3-benzotriazole have been determined. In earlier papers[1–4] studies on the interaction of the platinum group elements with 1:2:3-benzotriazole were reported.

The purposes of this study were to use the thermobalance as a means of detecting and following reactions in the solid state, of determining the degree of hydration and stability of hydrated and/or unhydrated forms of the osmium 1:2:3-benzotriazole co-ordination compounds.

EXPERIMENTAL

Apparatus and materials. The thermobalance employed in this study was assembled as described by WENDLANDT.[5] Temperature measurements of the furnace were obtained with an iron–constantan thermocouple using an ice bath as reference junction. The thermocouple was calibrated against the boiling point of water and the melting points of water, tin, lead and antimony; these materials were of 99·98 per cent or greater purity. A Fisher type S portable potentiometer was used to determine the voltage of the thermocouple. A synchronous motor-driven powerstat was employed to vary the voltage.

All precipitates were prepared according to the procedure of WILSON and BAYE[1] and were dried at room temperature for 24 hr in a desiccator containing magnesium perchlorate before being pyrolysed in the furnace of the thermobalance. Decomposition of the compounds was carried out by placing between 15 and 35 mg of each dried precipitate in the platinum boat and suspending the boat in the furnace. The motor-driven powerstat was set, initially, at 20 V and the input voltage was adjusted to 110 V by means of a second powerstat. The furnace temperature was increased at the rate of 5°/min. Readings on the balance and on the potentiometer were taken at short intervals until a temperature of 750°C was obtained.

Pyrolysis of $Os(OH)_3(C_6H_4NHN_2)_3$. A 29·4 mg sample of $Os(OH)_3(C_6H_4NHN_2)_3$ was used for the pyrolysis of this compound. On raising the temperature linearly at a rate of 5°/min, curve 1, in Fig. 1, was obtained with two horizontal portions corresponding to constant weight levels of

[1] R. F. WILSON and L. J. BAYE, *J. Amer. Chem. Soc.* **80**, 2652 (1958).
[2] R. F. WILSON and L. E. WILSON, *Analyt. Chem.* **28**, 93 (1956); *J. Amer. Chem. Soc.* **77**, 6204 (1955).
[3] R. F. WILSON, L. E. WILSON and L. J. BAYE, *J. Amer. Chem. Soc.* **78**, 2370 (1956).
[4] R. F. WILSON and C. M. WOMACK, *J. Amer. Chem. Soc.* **80**, 2065 (1958).
[5] W. W. WENDLANDT, *Analyt. Chem.* **27**, 1277 (1955).

$Os(OH)_2(C_6H_4NHN_2)_2$ and $Os_2O_3(C_6H_4NHN_2)_6$, respectively. From room temperature up to 200°C the hydroxy compound is stable and can be weighed as such. In the range 200°–230°C, the compound loses irreversibly one and one-half molecules of water per formula weight of $Os(OH)_2(C_6H_4NHN_2)_2$. From 230° to 400°C the plateau corresponds to $Os_2O_3(C_6H_4NHN_2)_6$. At 400°C a rapid decomposition of the compound took place and was complete at 410°; there was no residue remaining on the pan since osmium formed its volatile tetroxide.

Pyrolysis of $Ba_2[OsO_2(C_6H_4NHN_2)_4(H_2O)_2]_2$. Pyrolytic decomposition of a 23·8 mg sample of

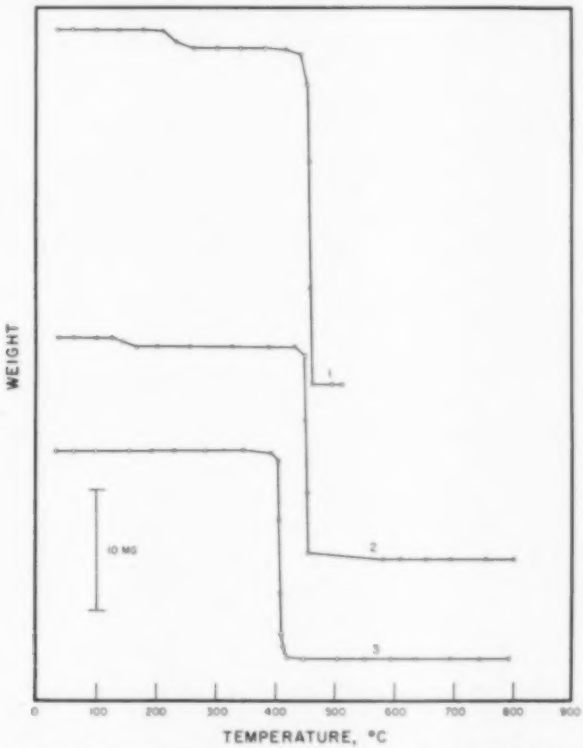

FIG. 1.—Thermal decomposition curves: curve 1, $Os(OH)_2(C_6H_4NHN_2)_2$: curve 2, $Ba_2[OsO_2(C_6H_4NHN_2)_4(H_2O)_2]_2$: curve 3, $K_2[OsO_2(C_6H_4NHN_2)_4]$.

the barium compound, Fig. 1, indicates losses in weight per formula weight of compound of four molecules of water between 130° and 150° and eight molecules of benzotriazole and one formula weight of Os_2O_3 between 427° and 450°C. The last plateau which persists up to the 850°C limit of this study corresponds to three formula weights of barium oxide.

Pyrolysis of $K_2[OsO_2(C_6H_4NHN_2)_4]$. The pyrolysis of a 20·8 mg sample of the potassium compound is shown in Fig. 1, exhibiting two horizontals. The change in weight per formula weight of compound between 390° and 420°C corresponds to the loss of four molecules of benzotriazole and $OsO_{1\cdot5}$ (or Os_2O_3 per two formula weights of the compound); the second horizontal corresponds to K_2O residue. The weight of the residue is constant up to at least 850°, but it picks up water on standing at room temperature.

Pyrolysis of $OsCl_2(C_6H_4NHN_2)_2$. Pyrolysis curve 1, Fig. 2, obtained from a 32·6 mg sample of the chloro compound was very similar in shape to the curve obtained from the bromo compound. However, the compound level for the chloro compound immediately following the removal of the three molecules of benzotriazole between 395° and 430°C was more pronounced than for the corresponding removal of benzotriazole in the bromo compound. After the plateau between 430° and 560°C, the decomposition of presumable osmium chloride takes place with explosive violence.

Pyrolysis of $OsBr_3(C_6H_4NHN_2)_3$. Pyrolysis of 19·7 mg of the bromo compound gave curve 2 shown in Fig. 2. A loss in weight was observed between 380° and 400°C which corresponded to the removal of three molecules of benzotriazole. Shortly after this loss another loss in weight was observed at 410°C which probably corresponded to the oxidative decomposition of osmium bromide.

Pyrolysis of $Na_2[OsO_2(C_6H_4NHN_2)_4(H_2O)_2]$. On raising the temperature linearly as in the foregoing procedure, a 20·7 mg sample of this compound gave pyrolysis curve 3 shown in Fig. 2, having three horizontals. The first decrease in weight between 130° and 150°C corresponds to the

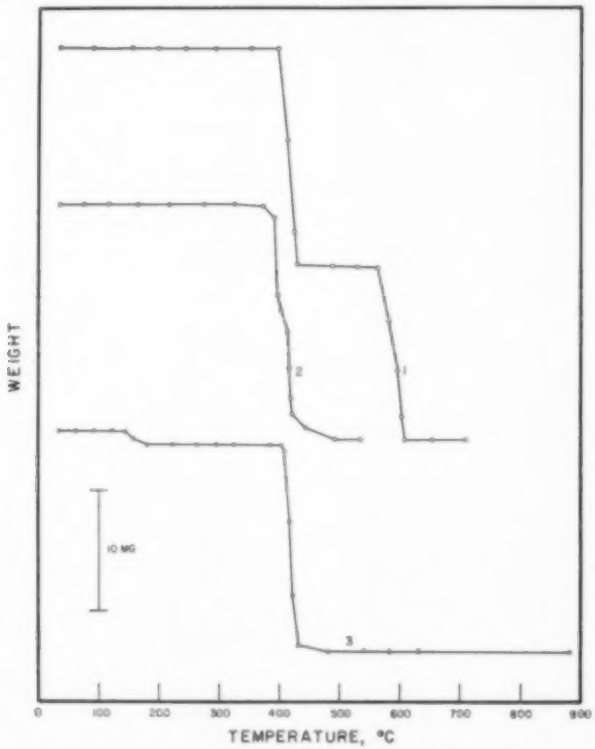

FIG. 2.—Thermal decomposition curves: curve 1, $OsCl_3(C_6H_4NHN_2)_3$: curve 2, $OsBr_3(C_6H_4NHN_2)_3$: curve 3, $Na_2[OsO_2(C_6H_4NHN_2)_4(H_2O)_2]$.

loss of two molecules of water. The second decrease in weight, 400°–420°C, corresponds to the loss of four molecules of benzotriazole and the Os_2O_3 function in the compound which went off as OsO_4. The residual weight corresponded to sodium oxide which is stable up to the 850°C temperature limit of this study. On standing at room temperature the residue picks up water and increases in weight. It is safe to weigh the compound as the hydrate up to 130°C and in the anhydrous form between 150° and 400°C.

Pyrolysis of $Pb_2[OsO_2(C_6H_4NHN_2)_4]_2$. The general shape of curve 1, in Fig. 3, for the pyrolysis of 34·2 mg of the lead compound is comparable to the one obtained from the pyrolysis of the previously described potassium compound. In the temperature range 400°–430°C, the loss in weight corresponds to eight molecules of benzotriazole. The weight of the residue, PbO, which remained after the decomposition, increased slightly on heating. This small gain in weight is probably caused by the formation of one or more higher oxides of lead.

Pyrolysis of $Ca_2[OsO_2(C_6H_4NHN_2)_4(H_2O)_2]_2$. The first loss in weight (curve 2, Fig. 3) for a 20·0 mg sample of the calcium compound occurs between 130° and 145°C by the removal of four molecules of water per formula weight of the compound. A second loss in weight takes place between 410° and 440°C and corresponds to the decomposition of the compound by the loss of eight molecules

of benzotriazole and one formula weight of Os_2O_3 (which escapes as OsO_4) per formula weight of the calcium compound. The third plateau corresponds to three formula weights of calcium oxide.

Pyrolysis of $Ag_2[OsO_2OH(C_6H_4NHN_2)_3]$. Pyrolysis data obtained from a 20·3 mg sample of the silver compound gave decomposition curve 3, Fig. 3, which is very similar to the curve obtained from the zinc compound. Weight relations indicated that six molecules of benzotriazole and one formula weight of Os_2O_3 per two formula weights of the silver compound were given off between 395° and 420°C. The residue consisted of two gram-atoms of silver per formula weight of compound.

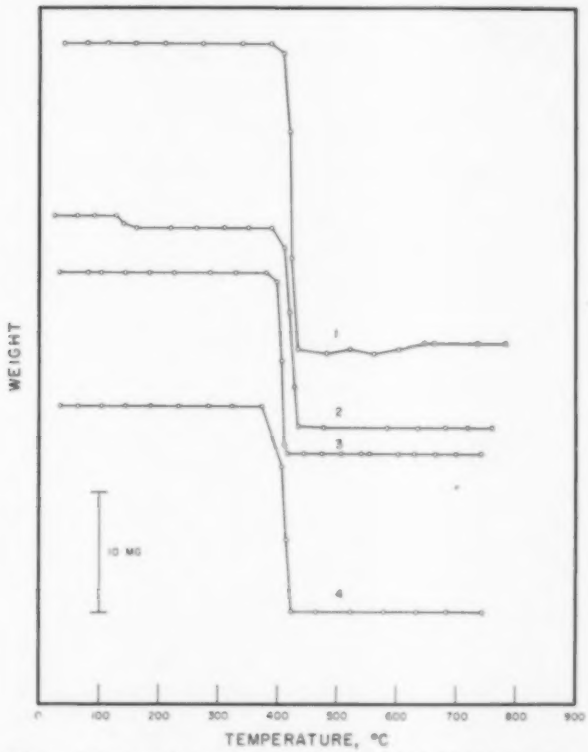

FIG. 3.—Thermal decomposition curves: curve 1, $Pb_2[OsO_2(C_6H_4NHN_2)_4]_2$: curve 2, $Ca_2[OsO_2(C_6H_4NHN_2)_4(H_2O)_2]_2$: curve 3, $Ag_2[OsO_2OH(C_6H_4NHN_2)_3]$: curve 4, $Zn[OsO_2OH(C_6H_4NHN_2)_4]$.

Pyrolysis of $Zn[OsO_2OH(C_6H_4NHN_2)_4]$. Pyrolysis of an 18·5 mg sample of this compound was carried out in the usual manner giving curve 4 in Fig. 3. The only loss in weight for this compound occurred between 400° and 420°C and corresponded to its decomposition by loss of eight molecules of benzotriazole and one formula weight of Os_2O_3 per two formula weights of compound. The residue corresponded to zinc oxide and was stable up to at least 850°C.

DISCUSSION

Thermogravimetric analytic data presented in this paper further support the proposed formulas of several osmium–1:2:3-benzotriazole compounds reported in a previous paper.[1] Final thermal decomposition or oxidation of the osmium–1:2:3-benzotriazole compounds in the temperature range 380°–560°C, gave osmium tetroxide, nitrogen, carbon dioxide, water, and in certain cases metallic oxides as products. The thermal decomposition curve of $Os(OH)_3(C_6H_4NHN_2)_3$ indicates

that the following irreversible reaction probably takes place between 200° and 230°C.

$$2Os(OH)_3(C_6H_4NHN_2)_3 \rightarrow Os_2O_3(C_6H_4NHN_2)_6 + 3H_2O$$

The compounds $Ca_3[OsO_3(C_6H_4NHN_2)_4(H_2O)_2]_2$ and $Ba_3[OsO_3(C_6H_4NHN_2)_4(H_2O)_2]_2$ when heated slightly above 120° and 130°C, respectively, may be represented by the following reversible reaction in which M is used in the place of calcium or barium.

$$M_3[OsO_3(C_6H_4NHN_2)_4(H_2O)_2]_2 \rightleftharpoons M_3[OsO_3(C_6H_4NHN_2)_4]_2 + 4H_2O$$

The pyrolysis curve of $Na_3[OsO_3(C_6H_4NHN_2)_4(H_2O)_2]$ indicates that between 130° and 150°C the following reaction takes place.

$$Na_3[OsO_3(C_6H_4NHN_2)_4(H_2O)_2] \rightleftharpoons Na_3[OsO_3(C_6H_4NHN_2)_4] + 2H_2O$$

In the temperature ranges 380°–400°C and 395°–430°C, the $OsBr_3(C_6H_4NHN_2)_3$ and the $OsCl_3(C_6H_4NHN_2)_3$ compounds, according to weight loss, give the following reaction in which X is used for chlorine or bromine.

$$OsX_3(C_6H_4NHN_2)_3 \rightarrow OsX_3 + 3C_6H_4NHN_2$$

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HEAT STABILITIES OF SOME LOW MELTING SCHIFF BASE CHELATES

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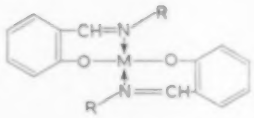
(*Received* 13 *June* 1958)

Abstract—The preparation of eleven new N-(*n*-alkyl)salicylaldimine zinc chelates is reported. The melting points of these compounds decrease greatly as the size of the alkyl group is increased, but none of the compounds are liquid at room temperature. The melting points of most of the zinc chelates are intermediate between those of the corresponding copper and nickel compounds. Heat stabilities of the zinc chelates were compared with those of the corresponding copper and nickel chelates. None of the substances examined were outstandingly heat stable. All of the chelates decompose at a significant rate at 200°C, with the copper compounds the least stable.

MODERN technology has created a need for liquid lubricants and hydraulic liquids having greater heat stability than materials now available. Some evidence exists that certain classes of metal chelate compounds possess high heat stability,[1] but little is known of the properties of metal chelates in the liquid state. Part of this lack of information is undoubtedly due to the fact that most of the metal chelates which have been reported have inconveniently high melting points. It has been shown, however, that known chelate molecules can sometimes be modified with alkyl substituents to give compounds having much lower melting points.[2,3,4]

In a previous paper[3] the synthesis of the copper and nickel N-alkylsalicylaldimine chelates I were described.



I

The melting points of these compounds were observed to decrease markedly with increase in chain length from methyl to *n*-tetradecyl. The present paper reports the synthesis of the corresponding zinc chelates I and compares their heat stabilities in air with those of the analogous copper and nickel compounds.

EXPERIMENTAL

Preparation of compounds

The copper and nickel chelates were prepared and purified as described previously.[3] The zinc chelates were prepared in an analogous manner. The following general procedure was used. To 6·1 g (0·05 mole) of salicylaldehyde dissolved in 100 ml of methanol was added 0·05 mole* of the appropriate amine, either as the pure compound or as a solution in water. The mixture was allowed to stand at room temperature for a few minutes and 2·0 g of NaOH in 50 ml of water were added. To the resulting clear solution was then added, slowly with rapid stirring, a solution of 0·025 mole

* A twofold excess of amine was used for the first two members of the series.

[1] R. P. LINSTEAD, *J. Chem. Soc.* 1027 (1934).
[2] G. F. MORGAN and E. HOLMES, *J. Chem. Soc.* **127**, 2891 (1925).
[3] R. G. CHARLES, *J. Org. Chem.* **22**, 677 (1957).
[4] R. G. CHARLES, *J. Inorg. Nucl. Chem.* **6**, 42 (1958).

$Zn(NO_3)_2$ in 100 ml of water. The zinc chelate precipitated during the latter addition.* The mixture was stirred for a few minutes at room temperature, heated briefly nearly to boiling and allowed to cool overnight in the refrigerator. The solid was filtered off, washed with water and dried in a vacuum desiccator at room temperature. Yields of the crude products were above 90 per cent of the theoretical value. The crude products, in at least some instances, appeared to contain some zinc hydroxide.

The chelates were all recrystallized, in most cases from methanol. In some instances supersaturation was observed during the recrystallization process and it was necessary to add water or to cool in dry ice to induce crystallization. In a few cases high zinc analyses were initially obtained for the purified compounds, evidently due to the presence of finely divided zinc hydroxide which passed through the filter paper during the recrystallizing procedure. This contaminant could be

TABLE 1.—ZINC N-(*n*-ALKYL)SALICYLALDIMINE CHELATES

R	m.p. (°C)	Zn (%)		N (%)		Molecular weight	
		Calc.	Found	Calc.	Found	Theor.	Found
Methyl	258–259	19·59	19·66	8·40	8·2[b]	333·7	[c]
Ethyl	152–153[a]	18·07	17·76	7·75	7·51	361·7	367
n-Propyl	138–139	16·77	16·82	7·19	7·12	389·8	[c]
n-Butyl	152–152·5	15·65	15·70	6·70	6·65	417·8	419
n-Amyl	88–90[a]	14·56	14·91	6·24	6·17	448·9	461
n-Hexyl	92·5–93·5	13·80	13·86	5·92	5·9[b]	474·0	485
n-Heptyl	98–99	13·02	13·14	5·55	5·49	502·0	[c]
n-Octyl	92–94	12·33	12·30	5·29	5·21	530·0	[c]
n-Decyl	82·5–83·5	11·15	11·09	4·78	4·4[b]	586·2	600
n-Dodecyl	89–90	10·18	10·20	4·34	4·34	642·3	[c]
n-Tetradecyl	85–86	9·37	9·16	4·01	4·14	698·4	[c]

[a] Recrystallized from tetrahydrofuran–petroleum ether. Others recrystallized from methanol or methanol–water.
[b] Determined by Kjeldahl method; others by Dumas method.
[c] Insufficiently soluble to form a 0·1 M solution at 11°C.

removed by filtering a solution of the compound in methanol or tetrahydrofuran through sintered glass. Analyses of the purified chelates are given in Table 1. All of the compounds are crystalline and pale yellow at room temperature. All were observed to give a strong blue fluorescence in the light from a mercury lamp. None of the chelates were observed to contain water of hydration when prepared as described.

Melting points

Melting points of the pure compounds were determined with a modified Hershberg apparatus and short range thermometers. Data are given in Table 1. Melting points of mixtures prepared from the pure compounds were determined in a similar manner. The temperature was raised very slowly and the temperature of final disappearance of solid was taken as the melting point. Mixtures of compounds were prepared by accurately weighing the two components into a glass vial. The vial was heated for 1·5 hr at 100°C (or where necessary for 0·5 hr at 160°C) and then cooled to room temperature overnight in a desiccator. The solid was then ground in a mortar and the melting point taken.

Molecular weights

Molecular weights were determined cryoscopically in 1,4-dioxane with a probable accuracy of ±5 per cent for the 0·1 M solutions used. A number of the chelates were not sufficiently soluble

* Some of the lower melting chelates first separated as oils which solidified on standing in the refrigerator.

at 11°C to permit the determination at this concentration. Results are listed in Table 1. All the chelates for which data were obtained are monomeric in dioxane within the accuracy of the determinations.

Heat stability determinations

Heat stabilities at 200°C were determined by heating 200 mg samples of the chelates contained in uncapped 5 ml glass vials in a constant temperature oven. The vials were removed at intervals,

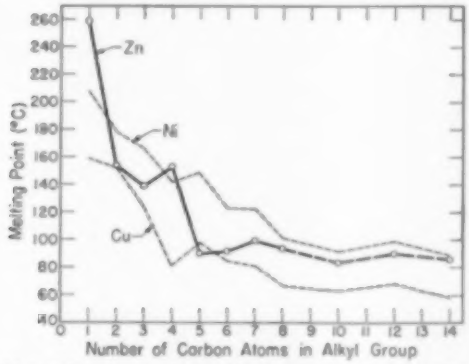


FIG. 1.—Melting point as a function of chain length for N-alkylsalicylaldimine chelates.

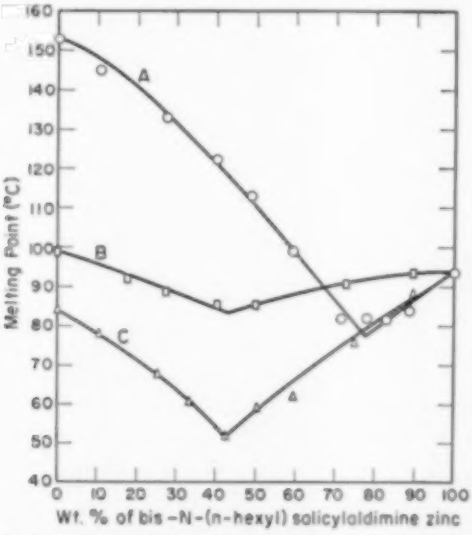


FIG. 2.—Melting points of mixtures of N-(*n*-alkyl)salicylaldimine zinc chelates.
A: *n*-hexyl and *n*-butyl
B: *n*-hexyl and *n*-heptyl
C: *n*-hexyl and *n*-decyl.

cooled in a desiccator and weighed. Heat stabilities at higher temperatures were determined, in a similar manner, by heating 200 mg of the samples in No. 00 porcelain crucibles in a constant temperature furnace. At the conclusion of many of the heat stability runs, the remaining organic material in the vial or crucible was decomposed with nitric acid and the residue then was ignited to the oxide. By this means it was possible to obtain an estimate of the metal lost during the heating period and hence the amount of the unchanged chelate which volatilized.* For the experiments at 300°C,

* It was assumed that none of the volatile decomposition products contained metal.

weight losses attributable to this cause were observed to be as much as 10 per cent of the total weight losses indicated in Fig. 4. Weight losses attributable to evaporation of the unchanged chelate were correspondingly lower at lower temperatures and were negligible at 200°C and 250°C. The weight loss values plotted in Fig. 4 are not corrected for the vaporization of chelate.

DISCUSSION OF RESULTS

Fig. 1 compares the melting points of the zinc chelates with those of the corresponding copper and nickel compounds. It will be observed that while the zinc N-methyl compound melts much higher than either the analogous copper or nickel chelate, the majority of the zinc chelates melt higher than the corresponding copper chelates but lower than the corresponding nickel compounds.

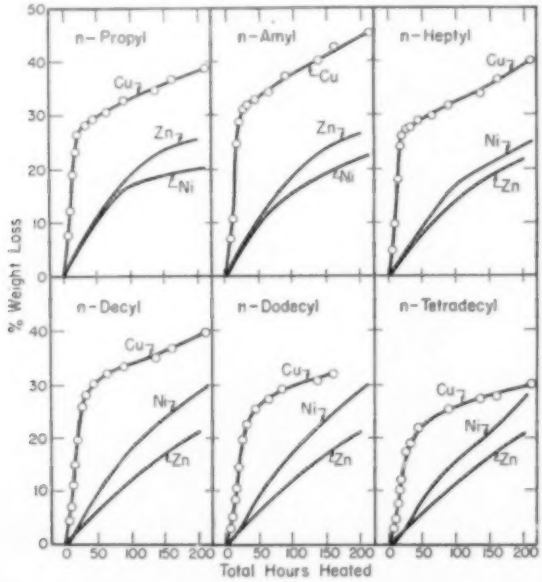


FIG. 3.—Weight loss curves for N-(*n*-alkyl)salicylaldimine chelates heated in air at 200°C. (For clarity experimental points are given only for the copper curves.)

A very marked decrease in melting point is observed when larger alkyl groups are substituted for methyl in each of the three N-methyl-salicylaldimine chelates. Even the lowest melting members of the three series, however, still melt too high to be of much practical value as fluids.

It was thought of interest to investigate the melting points of mixtures of the zinc chelates to determine whether any of these would have significantly lower melting points than the pure compounds. Mixtures were prepared from the *n*-hexyl compound with each of a number of other chelates from Table 1. Fig. 2 shows the melting point diagrams obtained for three of these systems. Similar diagrams were obtained also for mixtures of the *n*-hexyl chelate with the *n*-amyl, *n*-octyl, and *n*-dodecyl chelates.* Although many of the mixtures examined melt below the melting point of either component, all melt well above room temperature. It is interesting that the

* The temperatures and weight percentages of the *n*-hexyl chelate corresponding to the eutectic points in these diagrams are: *n*-amyl, 73°C, 53 per cent; *n*-octyl, 56°C, 42 per cent; *n*-dodecyl, 56°C, 42 per cent.

melting point diagrams obtained give no indication of the existence of unsymmetrical chelates in which the two *R* groups of formula I represent two different alkyl groups.

In Fig. 3 are plotted heat stability data at 200°C for a number of corresponding copper, nickel, and zinc salicylaldimine chelates. All of the chelates examined decompose to a significant extent under these conditions. In all cases the copper chelate was found to be the least stable. For the propyl and amyl compounds in Fig. 3, the zinc chelate was less stable than the nickel. For the heptyl, decyl, dodecyl,

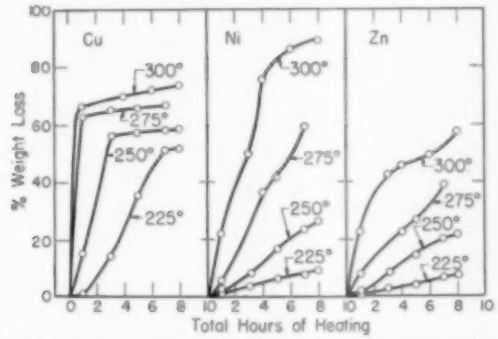


FIG. 4.—Weight loss curves for N-(*n*-dodecyl)salicylaldimine chelates heated in air.

and tetradecyl compounds, the opposite appears to be true (at least after the first few hours). All of the zinc chelates were observed to turn black after a few hours heating. Colour changes for the copper and nickel chelates could not be observed because of the very dark colours of the undecomposed compounds. Fig. 4 shows the effect of increase of temperature on the short-term decomposition of the three dodecylsalicylaldimine chelates.

It is interesting to compare the heat stability results obtained here with those reported by MARVEL *et al.*[5] These authors studied the heat stabilities of chelates similar to I but with the two nitrogen atoms bridged by organic groupings. The latter compounds were observed, for the most part, to decompose to a significant extent at 250°C, weight loss curves somewhat similar to those in Figs. 3 and 4 being obtained. Like the results found here, the copper chelates were found by MARVEL *et al.* to be less stable than the corresponding zinc and nickel compounds. The relative stabilities of corresponding zinc and nickel chelates were found by these workers to be dependent on the nature of the bridging group. Since all the data reported by MARVEL *et al.* refer to 250°C, a direct comparison with the present data is possible only for the dodecylsalicylaldimine chelates. The latter compounds appear to be somewhat less stable than those studied by the authors mentioned when comparison is made over the first few hours of heating.

Acknowledgement—The writer is grateful to Mrs. M. A. PAWLIKOWSKI for assistance in the experimental portion of this work.

[5] C. S. MARVEL, S. A. ASPEY and E. A. DUDLEY, *J. Amer. Chem. Soc.* **78**, 4905 (1956).

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THE SALTS OF ORGANIC PHOSPHORUS ACIDS—I

THE INFRA-RED SPECTRA OF SALTS OF DI-*n*-BUTYL PHOSPHATE

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(*Received* 12 *June* 1958)

Abstract—The infra-red spectra of a number of salts of di-*n*-butyl phosphate have been recorded and the results interpreted from a consideration of the interaction of the various groups in the di-*n*-butyl phosphate radical with the metal ion.

THE infra-red spectra of di-*n*-butyl phosphate, its silver salt and those of a number of similar aliphatic and aromatic phosphorus acids have been recorded by BELLAMY and BEECHER.[1] These authors pointed out that the usual position of the band for the P=O group in the 1200–1300 cm^{-1} region,[2] vanishes in all cases on formation of the silver salts and is replaced by a band in the 1050–1100 cm^{-1} region which was tentatively ascribed to the ionic phosphate vibration. Another assignment noted was that of the P—O—C vibration to the 1030 cm^{-1} region which may be regarded as arising essentially from the O—C link of the P—O—C skeleton whereas a band at 980 cm^{-1} arises from the P—O link.

The present investigation was carried out to determine the influence of the metal ion on the infra-red spectra of salts of di-*n*-butyl phosphate with a view to assessing the interaction of the various groups of the di-*n*-butyl phosphate radical with the metal ion concerned.

EXPERIMENTAL

The di-*n*-butyl phosphates of sodium, barium, lithium, manganese (II), copper (II) and nickel (II), were made by adding, in slight excess, their carbonates to an aqueous solution of dibutyl phosphate. Evaporation on a water bath after filtration yielded waxy deposits of the salt which were recrystallized. The remaining salts were relatively insoluble in water and were prepared by direct precipitation from an acidified nitrate solution of the metal ion. The resulting precipitates were washed with water, alcohol and finally a little ether and dried over phosphorus pentoxide for several weeks.

The infra-red spectra of the di-*n*-butyl phosphates in Nujol suspension were recorded on a Grubb–Parsons double beam instrument Model S4, with a rock-salt prism. A selection of the spectra obtained is shown in Fig. 1 and detailed by Table 1.

RESULTS AND DISCUSSION

1242–1124 cm^{-1} *region.* Bands due to the bonded P=O group have been assigned to this region occurring in the case of di-*n*-butyl phosphate[1] at 1220 cm^{-1}. On salt formation a band persists in this region though its position is dependent on the metal ion present, the positions being shown by Table 1. In the sodium salt the band appears at the highest frequency being shifted from the position at 1220 cm^{-1} due to the

[1] L. J. BELLAMY and L. BEECHER, *J. Chem. Soc.* 728 (1953).
[2] C. I. MEYRICK and H. W. THOMPSON, *J. Chem. Soc.* 225 (1950).

release of the P═O group from hydrogen bonding. In the barium and lithium salts the band is virtually in the same position. With the manganese salt a small shift to lower frequency occurs, the shift becoming more pronounced at nickel. It is proposed

TABLE 1

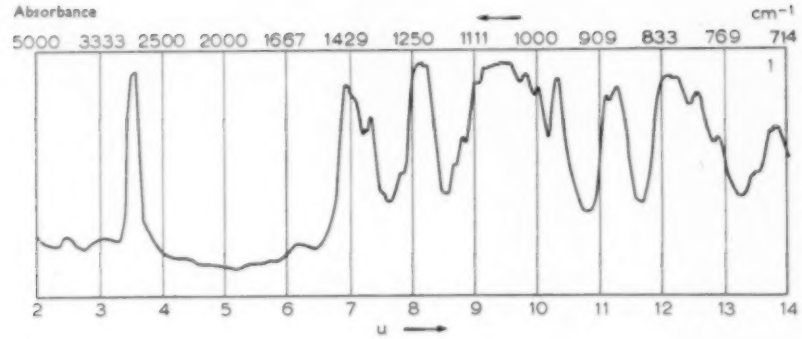
Metal salt	Position of P═O band (cm^{-1})
Sodium	1242
Barium	1227
Lithium	1242, 1212
Manganese (II)	1220
Copper (II)	1227
Nickel (II)	1190
Lead (II)	1190
Mercury (II)	1130
Mercury (I)	1183
Aluminium	1183
Lanthanum	1176
Yttrium	1190
Cerium (III)	1170
Iron (III)	1163
Cerium (IV)	1156
Thorium	1183
Bismuthyl	1124
Zirconyl	—
Uranium (VI)	1124

that this shift is due to the participation of the P═O group in bonding to the metal ion such that group represented as $P{=}O \rightarrow Me^{+n}$ appears. This tendency to form such a bond is then shown to some degree by the other metal ions with large shifts being shown in the lanthanum, ferric, ceric, mercuric, bismuthyl and uranyl salts, where the metal ion involves an ever increasing participation in bonding to the P═O group.

909–730 *cm^{-1} region.* The bands exhibited by the free acid in this region are very weak. However, those exhibited by the sodium and barium salts are intense. In the lithium salts these bands are diminished in intensity though little altered in position. This tendency is continued in most of the other salts being very weak in the zirconyl salt and almost non-existent in the uranyl salt. The aluminium and lanthanum salts show relatively strong bands in this region in contrast to the di-*n*-butyl phosphates of yttrium and cerium (III).

It is proposed that the appearance of these strong bands for the sodium and barium salts is due to the $P{-}O^{-}$ group. The loss in intensity of these bands in the remaining salts may be due to the formation of an electrostatic link with an increasingly covalent character which reaches a maximum in the uranyl salt where the $P{-}O^{-}{-}UO_2^{2+}$ bond is of the same order of covalency as the P—O—H bond resulting in the almost complete disappearance of the bands in this region.

1099–9524 cm^{-1} *region.* This region contains bands whose positions show little variation with change in the metal ion content of the salts, also in many cases the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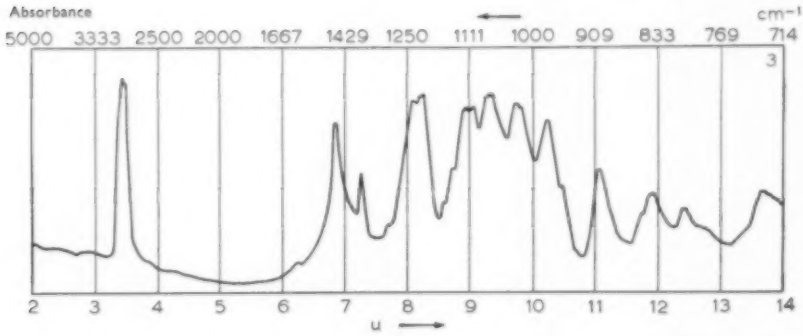
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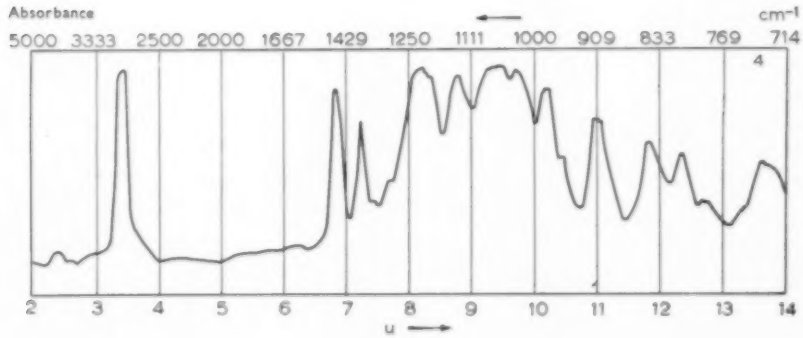
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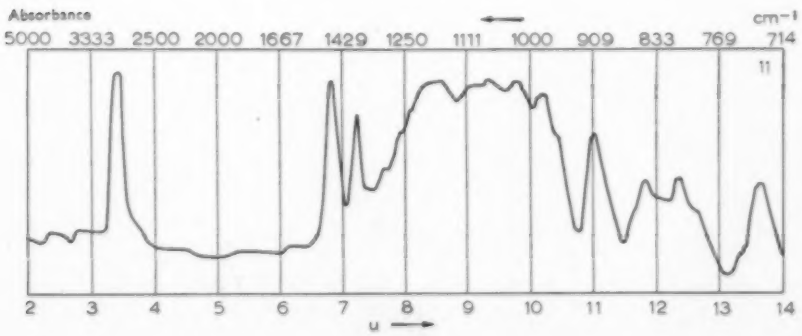
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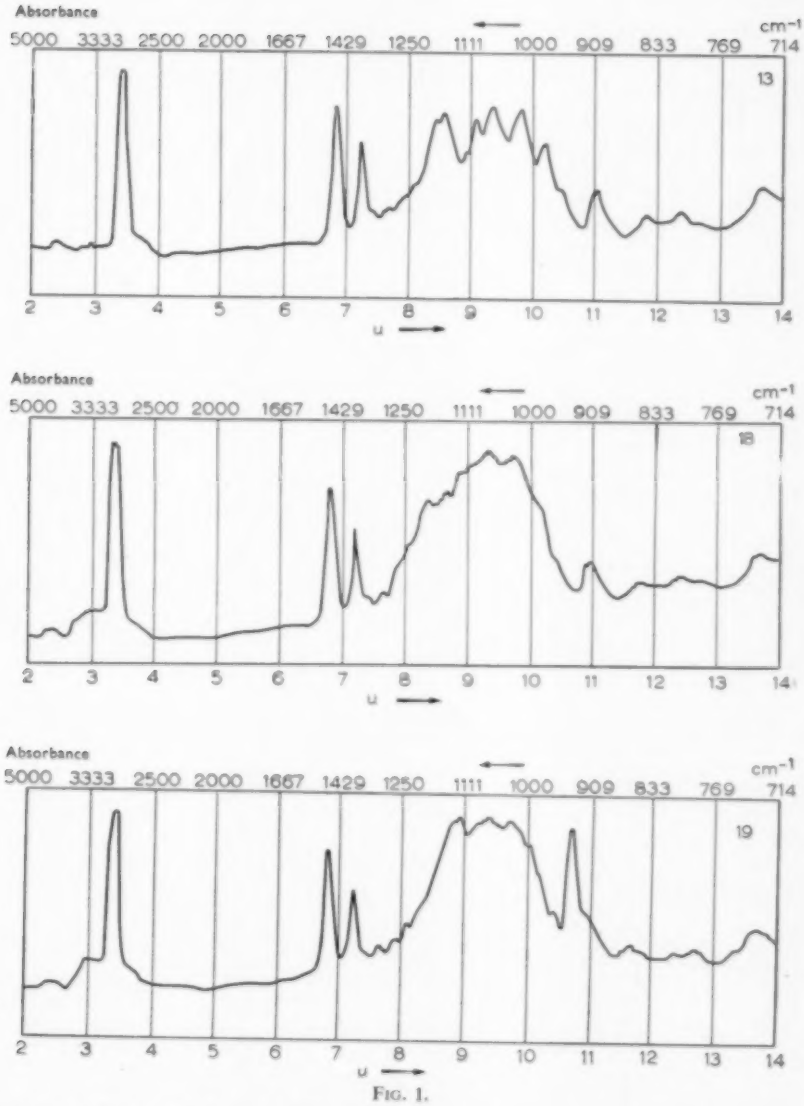

FIG. 1.

1—Sodium di-*n*-butyl phosphate; 3—Lithium di-*n*-butyl phosphate; 4—Manganese (II) di-*n*-butyl phosphate; 11—Lanthanum di-*n*-butyl phosphate; 13—Cerium (III) di-*n*-butyl phosphate; 18—Zirconyl di-*n*-butyl phosphate; 19—Uranium (VI) di-*n*-butyl phosphate.

resolution of these bands is poor. The band which appears in the region 1010 cm^{-1} in the sodium and barium salts appears as a shoulder absorption in the manganese (II), copper (II), nickel (II), lead (II), mercury (II) and aluminium salts but disappears in the remaining spectra, whilst the general appearance of the bands for these remaining salts is very similar.

The band in region 980 cm^{-1} persists in most of the salts studied; however in zirconyl dibutyl phosphate the band becomes almost indistinguishable whilst in uranyl dibutyl phosphate spectrum this band has disappeared. These two salts present exceptional behaviour which it is tentatively proposed is due to the interaction of the metal ion with the oxygen of the P—O—C group.

The infra-red spectra studies here indicate that the simplest structure is that presented by the sodium and barium salts which involve an essentially ionic link with the P—O^- group. The other salts studied point to the covalent character which this link may assume and to the interaction of the P=O group with the metal ion. Finally the possibility of bonding with the P—O—C group arises in the zirconyl and uranyl compounds.

Acknowledgements—The author expresses his gratitude to Messrs. ALBRIGHT and WILSON LTD. for the supply of di-*n*-butyl phosphate and to Miss N. CARAMANDO for recording the spectra.

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BASIC PROPERTIES OF THE DIOXIDES OF GROUP VI—I

SOLUTIONS OF SELENIUM DIOXIDE IN SULPHURIC ACID

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(*Received* 30 *June* 1958)

Abstract—Selenium dioxide dissolves in sulphuric acid and in oleum to give bright yellow solutions. It has been shown by means of conductivity and cryoscopic measurements that in such solutions selenium dioxide behaves as a weak base. It is partially ionized to give the $HSeO_2^+$ ion. Polymeric ions such as $HSe_2O_4^+$ are also present in these solutions. It appears that the un-ionized portion of the selenium dioxide forms compounds with sulphuric acid, e.g. $H_2SO_4 \cdot SeO_2$ and $H_2SO_4 \cdot Se_2O_4$, and with disulphuric acid, e.g. $H_2S_2O_7 \cdot SeO_2$. Tellurium dioxide was found to be insoluble in 100 per cent sulphuric acid and in oleum.

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IT has long been known that selenium dioxide dissolves in 100 per cent sulphuric and selenic acids to give bright yellow solutions.[1] A solution of selenium dioxide in sulphuric acid is often used as an oxidizing agent in organic chemistry.[2] However, apart from the work of HANTZSCH,[3] who measured the freezing-point depressions produced by selenium dioxide in sulphuric acid and concluded that it behaved as a monomeric non-electrolyte, there have been no investigations of the nature of solutions of selenium dioxide in sulphuric acid.

The dependence of the solubility of tellurium dioxide in dilute perchloric acid on the concentration of the acid has been attributed to the formation of TeO_2H^+.[4] That tellurium dioxide has basic properties is indicated by the formation of compounds with strong acids to which formulae such as the following have been attributed: $2TeO_2 \cdot SO_3$,[5] $2TeO_2 \cdot TeO_3$,[6] $2TeO_2 \cdot HNO_3$[7] and $2TeO_2 \cdot HClO_4$.[8] However, nothing is known of the structures of these compounds. It was the purpose of the present investigation to study the basic behaviour of the dioxides of Group VI by means of cryoscopic, conductimetric and other measurements on their solutions in some strong acid solvents. This paper describes the behaviour of selenium and tellurium dioxides in 100 per cent sulphuric acid and oleum.

Solutions of selenium dioxide in sulphuric acid

Cryoscopic measurements. The freezing-points listed in Table 1 (column 2) were obtained by interpolation from the results of three separate experiments in which the freezing-points of fifteen different solutions were measured. These interpolated

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(1) J. MEYER and M. LANGNER, *Ber. Dtsch. Chem. Ges.* **60**, 285 (1927).
(2) G. R. WAITKINS and C. W. CLARK, *Chem. Rev.* **36**, 235 (1945).
(3) A. HANTZSCH, *Z. Phys. Chem.* **61**, 257 (1907).
(4) R. SCHUMANN, *J. Amer. Chem. Soc.* **47**, 356 (1925).
(5) R. BRAUNER, *J. Chem. Soc.* **55**, 382 (1889).
(6) R. METZNER, *C. R. Acad. Sci., Paris* **124**, 32 (1897).
(7) P. KOTHNER, *Ann.* **319**, 15 (1901).
(8) F. FICHTER and M. SCHMID, *Z. Anorg. Chem.* **98**, 141 (1916).

freezing-points were corrected to allow for the repression of the self-dissociation of the solvent as described elsewhere.[9] The freezing-point depressions, θ (column 4) were calculated from these corrected freezing-points (column 3). The number of moles of particles, ν, produced in solution by one mole of solute may be calculated from the freezing-point depressions by means of the equation[10]

$$\theta/m_2 = 6{\cdot}12g\nu(1 - 0{\cdot}002\theta)[1 + (2s - \nu)m_2/20{\cdot}4] \quad (1)$$

where m_2 is the molality of the solute, s is the number of moles of sulphuric acid used

TABLE 1.—FREEZING-POINTS OF SOLUTIONS OF SELENIUM DIOXIDE IN SULPHURIC ACID

m_2	f.p.$_{obs.}$ (°C)	f.p.$_{corr.}$ (°C)	θ (°C)	ν	10^3K_b
0·00	10·365	10·515	0·150	—	—
0·04	10·064	10·128	0·387	1·58	3·9
0·05	9·990	10·047	0·468	1·53	3·6
0·06	9·917	9·969	0·546	1·49	3·3
0·07	9·848	9·895	0·620	1·44	2·8
0·08	9·778	9·822	0·693	1·42	2·7
0·09	9·707	9·748	0·767	1·39	2·5
0·10	9·641	9·678	0·837	1·36	2·2
0·11	9·576	9·612	0·903	1·35	2·3
0·12	9·512	9·546	0·969	1·32	2·0
0·13	9·453	9·485	1·030	1·29	1·7
0·14	9·396	9·426	1·089	1·27	1·6
0·15	9·341	9·369	1·146	1·24	1·3

up by the ionization or reaction of one mole of the solute and g is the osmotic coefficient of the solvent. In the present case we may with sufficient accuracy put $g = 1$ and $s = 1$ (see equation 2). Values of ν obtained from the above equation are given in Table 1.

Conductivity measurements. The results of conductivity measurements on solutions of selenium dioxide in 100 per cent sulphuric acid at 25° are given in Fig. 1, together with values for solutions of potassium hydrogen sulphate[11] for comparison. Interpolated values at round concentrations of the conductivities at 10°, 25° and 40° are given in Table 2. The number of moles of hydrogen sulphate ions (γ) produced by one mole of an electrolyte E can be found to a good approximation by comparing the concentrations of solutions of the electrolyte and a fully ionized mono-hydrogen sulphate, e.g. $KHSO_4$, that have the same conductivities.[12] Thus $\gamma = c_E^{\kappa}/c_{KHSO_4}^{\kappa}$, where the superscript κ denotes that the solutions have the same conductivity and where the c's are concentrations in *molar* units. For a weak base γ is equal to the degree of ionization α. For our present purpose it is sufficiently accurate to use the

[9] R. J. GILLESPIE, S. J. BASS and E. A. ROBINSON, *J. Chem. Soc.* To be published. See also references (10) and (13).
[10] R. J. GILLESPIE and J. V. OUBRIDGE, *J. Chem. Soc.* 80 (1956).
[11] R. H. FLOWERS and R. J. GILLESPIE, *J. Chem. Soc.* (1958).
[12] R. J. GILLESPIE and C. SOLOMONS, *J. Chem. Soc.* 1796 (1957).

approximate expression $\gamma = m_E^{\kappa}/m_{KHSO_4}^{\kappa}$, where the m's are concentrations in *molal* units.

Ionization of selenium dioxide as a weak base. Reference to Table 1 shows that the values of ν for solutions of selenium dioxide in 100 per cent sulphuric acid decrease from 1·58 at 0·04 mole to 1·25 at 0·15 mole. From Table 2 it can be seen that γ

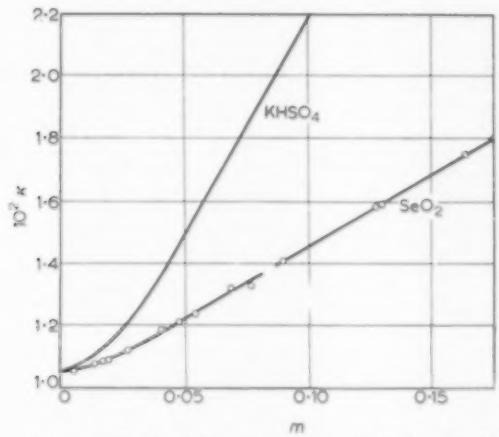


FIG. 1.—Conductivities of solutions of selenium dioxide.

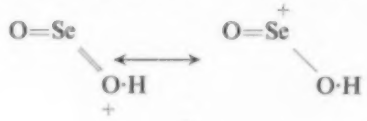
TABLE 2.—CONDUCTIVITIES OF SOLUTIONS OF SELENIUM DIOXIDE IN 100 PER CENT SULPHURIC ACID AT 10°, 25° AND 40°C

m_2	$\kappa \times 10^2$			γ	10^2K_b
	10°	25°	40°		
0·03	0·630	1·132	1·800	0·63	4·6
0·04	0·666	1·172	1·850	0·59	4·5
0·05	0·700	1·220	1·900	0·54	4·1
0·06	0·735	1·270	1·953	0·51	4·0
0·07	0·770	1·313	2·008	0·49	4·0
0·08	0·806	1·360	2·072	0·48	4·1
0·09	0·840	1·405	2·132	0·47	4·3
0·10	0·875	1·448	2·192	0·46	4·4
0·11	0·910	1·515	2·255	0·45	4·5
0·12	0·945	1·542	2·320	0·44	4·5
0·13	0·980	1·590	2·384	0·43	4·6
0·14	1·014	1·634	2·448	0·43	4·8
0·15	1·050	1·684	2·512	0·43	5·1

decreases from 0·63 to 0·43 over the same concentration range. It was found to be independent of temperature in the range 10° to 40°C. The simplest interpretation of these results is that selenium dioxide is a weak base, and is partially protonated according to the equation:

$$SeO_2 + H_2SO_4 \rightleftharpoons SeO_2H^+ + HSO_4^- \qquad (2)$$

forming the $HSeO_2^+$ ion which may be formulated as the resonance hybrid I.



(I)

A number of other possible reactions are inconsistent with our results. Thus, for example, the formation of a complex acid of selenium (IV) [cf. $HB(HSO_4)_4$ and $H_2Pb(HSO_4)_6$,[13,14]] or its ions, would give larger values of ν than were observed:

	ν	γ	
$SeO_2 + 8H_2SO_4 = H_2Se(HSO_4)_6 + 2H_3O^+ + 2HSO_4^-$	5	2	(3)
$SeO_2 + 7H_2SO_4 = HSe(HSO_4)_6^- + 2H_3O^+ + HSO_4^-$	4	1	(4)
$SeO_2 + 6H_2SO_4 = Se(HSO_4)_6^{2-} + 2H_3O^+$	3	0	(5)

The formation of the oxy-cation SeO^{2+}, the cation $SeO{\cdot}HSO_4^+$ and the un-ionized hydrogen sulphate $SeO(HSO_4)_2$ can also be rejected on similar grounds.

	ν	γ	
$SeO_2 + 3H_2SO_4 = SeO^{2+} + H_3O^+ + 3HSO_4^-$	5	3	(6)
$SeO_2 + 3H_2SO_4 = SeO{\cdot}HSO_4^+ + H_3O^+ + 2HSO_4^-$	4	2	(7)
$SeO_2 + 3H_2SO_4 = SeO(HSO_4)_2 + H_3O^+ + HSO_4^-$	3	1	(8)

The formation of selenious acid fits the conductivity results reasonably well, but not the cryoscopic results, and is in any case unlikely.

$$\left.\begin{aligned} SeO_2 + 2H_2SO_4 &= H_2SeO_3 + H_2S_2O_7 \\ H_2S_2O_7 + H_2SO_4 &\rightleftharpoons H_3SO_4^+ + HS_2O_7^- \end{aligned}\right\} \begin{matrix} 3 > \nu > 2 \\ 1 > \gamma > 0 \end{matrix} \qquad (9)$$

Moreover, the results given in Table 3 show that addition of potassium sulphate to solutions of SeO_2 or vice versa increases the freezing-point depression. This shows that selenium dioxide is not producing the $H_3SO_4^+$ ion since in that case potassium

TABLE 3.—FREEZING-POINTS OF SOLUTIONS OF SELENIUM DIOXIDE AND POTASSIUM SULPHATE IN SULPHURIC ACID

$10^3 m_{SeO_2}$	$10^3 m_{KHSO_4}$	f.p. (°C)	$10^3 m_{SeO_2}$	$10^3 m_{KHSO_4}$	f.p. (°C)
0·00	0·00	10·365	0·00	0·00	10·365
1·07	0·00	10·277	0·00	2·60	9·830
4·61	0·00	10·020	0·00	4·50	9·375
10·35	0·00	9·615	0·14	4·50	9·363
15·12	0·00	9·337	2·21	4·50	9·209
15·12	2·88	8·694	5·88	4·50	8·937
15·12	4·31	8·365	8·85	4·50	8·715
15·12	6·37	7·874	11·60	4·50	8·539

[13] R. H. FLOWERS, R. J. GILLESPIE and J. V. OUBRIDGE, *J. Chem. Soc.* 1925 (1956).
[14] R. J. GILLESPIE and E. A. ROBINSON, *Proc. Chem. Soc.* 145 (1957).

hydrogen sulphate would produce little or no change in the freezing-point as a consequence of the neutralization reaction:

$$H_3SO_4^+ + HSO_4^- = 2H_2SO_4 \qquad (10)$$

The formation of a compound $2SeO_2{\cdot}SO_3$ analogous to $2TeO_2{\cdot}SO_3$,[5]

$$2SeO_2 + 2H_2SO_4 = 2SeO_2{\cdot}SO_3 + H_3O^+ + HSO_4^- \qquad \nu = 1{\cdot}5,\ \gamma = 0{\cdot}5 \qquad (11)$$

would, if it were un-ionized, fit our results fairly well, except that the decrease of ν and γ from values greater than predicted by equation (11) to values less than predicted would remain unexplained. The results obtained in oleum solutions (p. 161) also provide evidence against this mode of ionization.

We may conclude with reasonable certainty that selenium dioxide undergoes partial protonation in accordance with equation (2). The degree of ionization, α, can be obtained from both the cryoscopic and conductimetric results. Thus $\alpha = \nu - 1$ and $\alpha = \gamma$. The basic dissociation constant K_b has been calculated from the expression.

$$K_b = \alpha \cdot m_{HSO_4^-}/(1 - \alpha) \qquad (12)$$

where $m_{HSO_4^-}$ is the *total* concentration of hydrogen sulphate ion including that remaining from the partially unrepressed solvent self-dissociation.

TABLE 4.—CALCULATION OF THE BASIC DISSOCIATION CONSTANT OF SELENIUM DIOXIDE

m_2	$1 - \alpha - 2\beta$	α	β	$m_{HSO_4^-}$	10^3K_b
0·04	0·38	0·58	0·02	0·0310	4·7
0·05	0·41	0·53	0·03	0·0342	4·4
0·06	0·41	0·48	0·05	0·0381	4·5
0·07	0·40	0·44	0·08	0·0415	4·5
0·08	0·42	0·42	0·08	0·0448	4·5
0·09	0·43	0·38	0·09	0·0477	4·3
0·10	0·42	0·36	0·11	0·0513	4·4
0·11	0·43	0·35	0·11	0·0546	4·4
0·12	0·42	0·32	0·13	0·0578	4·3
0·13	0·41	0·29	0·15	0·0608	4·3
0·14	0·38	0·27	0·17	0·0650	4·4
0·15	0·38	0·24	0·19	0·0678	4·1
				Mean =	4·4

Formation of polymeric ions. It may be seen that the K_b values obtained from conductivity results (Table 2) are reasonably constant, but those obtained from cryoscopy (Table 1) decrease with increasing concentration, and are always lower than the conductimetric values. This can be accounted for if it is assumed that on protonation the polymeric chain structure of selenium dioxide[15] is not completely broken down into its monomeric units, and that in addition to the ion $HSeO_2^+$ there are other mono-protonated species present, such as $HSe_2O_4^+$. If the stoicheiometric concentration of SeO_2 is m, if αm is the concentration of $HSeO_2^+$ and βm the concentration of $HSe_2O_4^+$, and if it is assumed that no other polymeric species are

[15] J. D. McCULLOUGH, *J. Amer. Chem. Soc.* **59**, 789 (1937).

present, the concentration of un-ionized SeO_2 is $(1 - \alpha - 2\beta)m$, and that of the hydrogen sulphate ion produced by the ionization is $(\alpha + \beta)m$. Hence $\nu = \alpha + 1$ and $\gamma = \alpha + \beta$. From the values of ν and γ given in Tables 1 and 2, the concentrations of $HSeO_2^+$, $HSe_2O_4^+$, HSO_4^- and un-ionized SeO_2 may all be calculated. Values thus obtained are given in Table 4. Values of K_b calculated from the expression

$$K_b = m_{HSeO_2^+} \cdot m_{HSO_4^-}/m_{SeO_2} \tag{13}$$

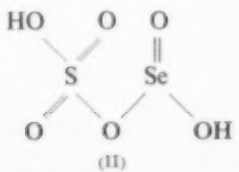
are also given in Table 4. These values are independent of concentration and give a mean value of $K_b = 4{\cdot}4 \times 10^{-2}$. In these dilute solutions $HSe_2O_4^+$ is probably the only polymeric ion present in appreciable concentrations.

TABLE 5.—CONDUCTIVITIES OF SOLUTIONS OF SeO_2 IN OLEUM AT 25°C

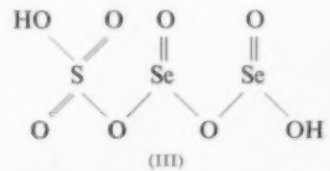
$m^f_{H_2S_2O_7}$	$r_{SeO_2}/m^f_{H_2S_2O_7}$	10^2K
0·2469	0·000	2·044
—	0·287	1·692
—	0·974	1·260
—	1·373	1·318
0·1400	0·000	1·670
—	0·383	1·378
—	0·786	1·213
—	0·936	1·193
—	1·002	1·190
—	1·069	1·191
—	1·194	1·202
—	1·599	1·312
0·0729	0·000	1·364
—	0·131	1·305
—	0·427	1·206
—	0·831	1·141
—	0·966	1·135
—	1·019	1·135
—	1·185	1·141
—	1·503	1·178

It seems likely that un-ionized selenium dioxide is present in solution not as SeO_2 molecules but as selenious–sulphuric acids, e.g. II and III. Evidence has been obtained for similar compounds with disulphuric acid (see p. 163). The ionization reaction producing $HSe_2O_4^+$ would then be more correctly written

$$H_2SeSO_6 = HSeO_2^+ + HSO_4^- \tag{14}$$



(II)



(III)

rather than as a simple protonation of SeO_2. The effect of un-ionized complex acids containing more than one selenium atom, e.g. III, should strictly be allowed for in the

above calculations, but there is insufficient experimental evidence to enable this to be done. The constancy of the calculated values of K_b suggests that such un-ionized polymeric acids are probably present in rather small amounts, and that their effect is rather unimportant.

Solutions of selenium dioxide in oleum and the acid $HB(HSO_4)_4$

Conductivity measurements. Some further confirmation of the conclusions reached above can be obtained from a consideration of the results of measurements made on

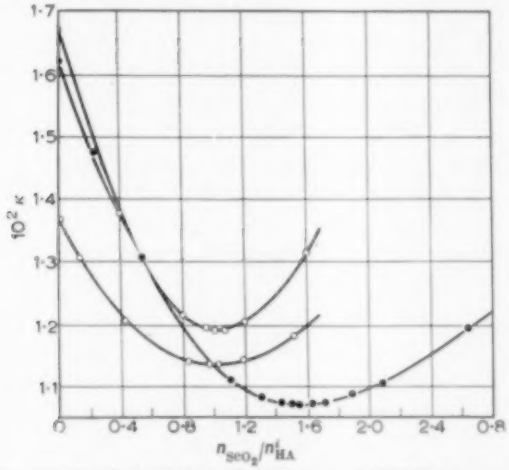


FIG. 2.—Conductimetric titrations of the acids $H_2S_2O_7$ and $HB(HSO_4)_4$ with selenium dioxide: ○ $H_2S_2O_7$, ● $HB(HSO_4)_4$.

solutions of selenium dioxide in dilute oleums and in solutions of the strong acid tetra(hydrogensulphato)boric acid in sulphuric acid. It may be seen from Table 5 and Fig. 2 that the conductivity decreases on the addition of selenium dioxide to a dilute oleum, and passes through a minimum at approximately the mole ratio $n_{SeO_2}/n^i_{H_2S_2O_7} = 1{\cdot}0$, where n_{SeO_2} is the number of moles of SeO_2 added and $n^i_{H_2S_2O_7}$ is the initial number of moles of $H_2S_2O_7$. This shows at once that the compound $2SeO_2{\cdot}SO_3$ is not being formed since in this case a minimum conductivity would be expected at the mole ratio 2·0.

$$2SeO_2 + H_2S_2O_7 = 2SeO_2{\cdot}SO_3 + H_2SO_4 \qquad (15)$$

On addition of selenium dioxide to a solution of $HB(HSO_4)_4$* in sulphuric acid a similar minimum conductivity is observed at the mole ratio SeO_2/initial $HB(HSO_4)_4 = 1{\cdot}6$ (Table 6, Fig. 2).

The simplest interpretation of these results is that selenium dioxide is a weak base, and that the experiments given in Tables 5 and 6 and Fig. 2 are in effect conductimetric titrations of the acids $H_2S_2O_7$ and $HB(HSO_4)_4$.[16]

$$H_2S_2O_7 + SeO_2 = HSeO_2^+ + HS_2O_7^- \qquad (17)$$

$$HB(HSO_4)_4 + SeO_2 = HSeO_2^+ + B(HSO_4)_4^- \qquad (18)$$

* Solutions of the strong acid $HB(HSO_4)_4$ in sulphuric acid are obtained by adding boric acid to an oleum solution so that the equation

$$H_3BO_3 + 3H_2S_2O_7 = HB(HSO_4)_4 + 3H_2SO_4$$

is satisfied.[12]

[16] R. J. GILLESPIE and E. A. ROBINSON, *J. Chem. Soc.* To be published. See also reference 13.

In such a titration the concentration of $H_3SO_4^+$ ions resulting from the ionization of the acid is decreased on the addition of the base (SeO_2) and the conductivity decreases correspondingly, finally passing through a minimum and increasing again on the

TABLE 6.—CONDUCTIMETRIC TITRATION OF $HB(HSO_4)_4$ WITH SeO_2 AT 25°C

$n^i_{HB(HSO_4)_4}$	$r_{SeO_2} n^i_{HB(HSO_4)_4}$	10^2K
0·510	0·000	1·620
	0·213	1·476
	0·528	1·307
	1·104	1·110
	1·301	1·081
	1·430	1·074
	1·498	1·071
	1·539	1·070
	1·624	1·070
	1·712	1·074
	1·884	1·086
	2·082	1·104
	2·638	1·191

addition of sufficient base to give rise to excess HSO_4^- ions. The position of the minimum conductivity is determined by the strengths of the acid and base and by the relative mobilities of the $H_3SO_4^+$ and HSO_4^- ions. It has been shown[16] that the minimum conductivity in a titration of $H_2S_2O_7$ occurs at a ratio of moles of added base to initial moles of acid $n_b/n_a^i = 0{\cdot}56(1 + 0{\cdot}017/K_b)$ where K_b is the dissociation

TABLE 7.—PREDICTED POSITIONS OF THE CONDUCTIVITY MINIMUM AND THE CORRESPONDING VALUES OF ν IN THE "TITRATIONS" OF THE ACIDS $H_2S_2O_7$ AND $H_2S_2O_7$ WITH SELENIUM DIOXIDE

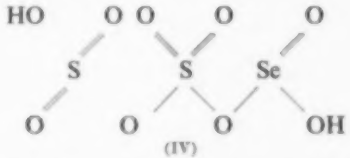
	$H_2S_2O_7$		$HB(HSO_4)_4$
	n_b/n_a^i at cond. min.	ν at $n_b/n_a^i = 1$	n_b/n_a^i at cond. min.
Strong base SeO_2 ($K_b = \infty$)	0·56	2·00	0·98
Weak base SeO_2 ($K_b = 0{\cdot}044$)	0·78	2·00	1·38
Un-ionized complex $SeO_2{\cdot}H_2S_2O_7$ or $SeO_2{\cdot}HB(HSO_4)_4$	1·00	1·00	1·00
Strong base Se_2O_4 ($K_b = \infty$)	1·12	1·50	1·96
Weak base Se_2O_4 (e.g. $K_b = 0{\cdot}044$)	1·56	1·50	2·76
Un-ionized complex $Se_2O_4{\cdot}H_2S_2O_7$ or $Se_2O_4{\cdot}HB(HSO_4)_4$	2·00	1·00	2·00
Observed	1·00	1·16–1·33	1·6

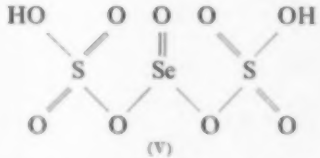
constant of the base. Substituting the value $K_b = 4{\cdot}4 \times 10^{-2}$ for SeO_2 gives $n_b/n_a^i = 0{\cdot}78$. The minimum conductivity in a titration of $HB(HSO_4)_4$ should occur at $n_b/n_a^i = 0{\cdot}98(1 + 0{\cdot}017/K_b) = 1{\cdot}38$ for $K_b = 4{\cdot}4 \times 10^{-2}$.

The differences between the predicted and observed positions of the minima can probably be attributed to (a) the formation of un-ionized complexes such as $SeO_2{\cdot}H_2S_2O_7$ (IV) and $SeO_2{\cdot}HB(HSO_4)_4$ and (b) to the formation of polymeric ions such as

$HSe_2O_4^+$. Thus (a) would give a conductivity minimum at $n_b/n_a^i = 1{\cdot}0$ while for (b) the position of the minimum would depend on the basicity of Se_2O_4, which is not known but is in any case at values of $n_b/n_a^i > 1{\cdot}0$ (Table 7). It seems necessary to consider both (a) and (b), because although the position of the minimum in the oleum titrations could in principle be accounted for entirely in terms of (a), i.e. the formation of the complex $SeO_2{\cdot}H_2S_2O_7$, it would have to be formed quantitatively, with no formation of $HSeO_2^+$, and this seems unlikely. In the case of the $HB(HSO_4)_4$ titrations, it can be seen from Table 7 that it is necessary to assume the occurrence of (b).

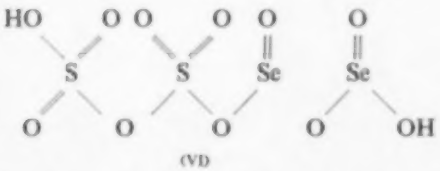
Cryoscopic measurements. Some further information is provided by the results of cryoscopic measurements on solutions of SeO_2 in oleum the results of which are given in Table 8.

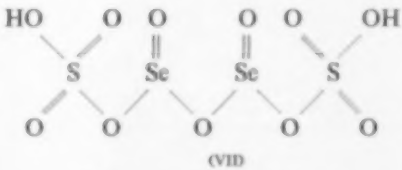

(IV)


(V)

For the simple reaction (17), the value of ν at the composition $n_{SeO_2}/n^i_{H_2S_2O_7} = 1{\cdot}0$ is necessarily 2·0 independently of the degree of ionization. From the freezing-points given in Table 7 values of the freezing-point at this composition were interpolated and corresponding values of ν were calculated from equation (1) with $s = 0$ (Table 8). The freezing-point depressions θ given in this table were calculated from the observed maximum freezing-point of sulphuric acid (10·37)° since at the minimum of an acid base titration the concentration of self-dissociation ions is very nearly equal to that in 100 per cent H_2SO_4.[16] These values decrease from 1·33 to 1·16 with increasing concentration of the oleum and are therefore not consistent with the simple ionization (17). If the possibility of the formation of an un-ionized complex $H_2S_2O_7{\cdot}SeO_2$ is taken into account, values of ν between 1·0 and 2·0 would be expected, depending on the extent of formation of the complex. The effect of polymeric ions such as $HSe_2O_4^+$ would also be to lower the value of ν. Thus quantitative formation of $HSe_2O_4^+$ would give $\nu = 1{\cdot}5$, while the formation of the corresponding un-ionized $Se_2O_4{\cdot}H_2S_2O_7$ (VI) or (VII) would give $\nu = 1{\cdot}0$ at the composition $n_{SeO_2}/n^i_{H_2S_2O_7} = 1{\cdot}0$ (Table 7).

$$2SeO_2 + H_2S_2O_7 = \underbrace{Se_2O_4{\cdot}H_2S_2O_7 + H_2S_2O_7}_{\nu = 1{\cdot}0} = \underbrace{HSe_2O_4^+ + HS_2O_7^- + H_2S_2O_7}_{\nu = 1{\cdot}5} \qquad (19)$$


(VI)


(VII)

To account for the observed values of ν it is necessary to assume that (a) is of some importance in oleum solutions. We may summarize the behaviour of selenium dioxide in dilute solutions in oleum by means of the equations

$$SeO_2 + H_2S_2O_7 = SeO_2{\cdot}H_2S_2O_7 = SeO_2H^+ + HS_2O_7^- \qquad (20)$$

$$2SeO_2 + H_2S_2O_7 = Se_2O_4{\cdot}H_2S_2O_7 = Se_2O_4H^+ + HS_2O_7^- \qquad (21)$$

The behaviour of selenium dioxide in solutions of the acid $HB(HSO_4)_4$ can probably be represented by similar equations, but since the minimum conductivity is observed at $n_b/n_a^i = 1{\cdot}6$ and the formation of $SeO_2{\cdot}HB(HSO_4)_4$ would lead to a conductivity minimum at $n_b/n_a^i = 1{\cdot}0$, there is no evidence for the formation of such an intermediate un-ionized complex. However, no certain conclusions can be reached in the absence of appropriate cryoscopic measurements.

Table 8.—Freezing-points of solutions of selenium dioxide in dilute oleums

$m^i_{H_2S_2O_7}$	$r_{SeO_2}/m^i_{H_2S_2O_7}$	f.p. (°C)	$m^i_{H_2S_2O_7}$	$r_{SeO_2}/m^i_{H_2S_2O_7}$	f.p. (°C)
0·080	0·000	9·832	0·172	0·000	9·212
	0·201	9·830		0·013	9·207
	0·354	9·820		0·093	9·199
	0·718	9·782		0·325	9·177
	1·078	9·707		0·776	9·094
	1·506	9·625		0·876	9·060
	2·060	9·511		0·987	9·030
0·102	0·000	9·698		1·000	9·029
	0·309	9·672		1·046	9·018
	1·361	9·468		1·096	8·997
	1·594	9·368		1·121	8·985
	2·593	9·009		1·336	8·897
	3·070	8·815		1·503	8·828
	3·461	8·657		2·023	8·560
0·131	0·000	9·451		2·513	8·318
	0·186	9·421	0·2630	0·000	8·563
	0·471	9·405		0·045	8·579
	0·979	9·318		0·125	8·599
	1·450	9·163		0·196	8·614
	1·932	8·980		0·288	8·625
	2·305	8·819		0·411	8·620
				0·663	8·595
				0·911	8·538
				1·264	8·396

It may be noted that it is possible to formulate the un-ionized complexes $SeO_2{\cdot}H_2S_2O_7$ and $Se_2O_4{\cdot}H_2S_2O_7$ in two ways; thus the former may be selenious disulphuric acid (IV) or selenoxydi(hydrogensulphate) $SeO(HSO_4)_4$ (V) and $Se_2O_4{\cdot}H_2S_2O_7$ may similarly be (VI) or (VII). It is not possible to distinguish between them on the basis of the present measurements. If we assume that all these compounds are in fact sulphates rather than disulphates, the relations between them and the corresponding oxides and hydroxides (acids) are shown in Fig. 3.

Tellurium dioxide

An attempt was made to measure the conductivities of solutions of tellurium dioxide in sulphuric acid and oleum but it was found to be very insoluble and no change in the conductivity of either sulphuric acid or oleum was detectable after it had been in contact with solid tellurium dioxide for several days. It seems quite likely,

by analogy with the behaviour of selenium dioxide, that a sulphate is formed e.g. $TeO(OH)(SO_4H)$ or $Te_2O_3(OH)(SO_4H)$ but that it is polymeric and insoluble in sulphuric acid. The compound $2TeO_2 \cdot SO_3$ can be formulated as $Te_2O_3 \cdot SO_4$ and the

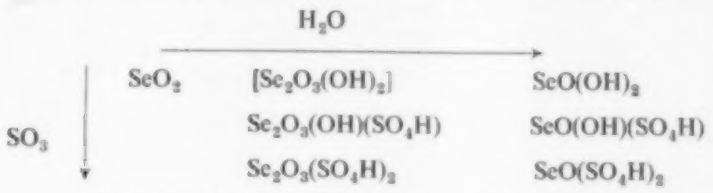


FIG. 3—Oxy-, hydroxy- and sulphato-compounds of selenium (IV).

compounds with other strong acids, e.g. $2TeO_2 \cdot HNO_3$ and $2TeO_2 \cdot HClO_4$ can similarly be formulated as derivatives of ditellurous acid $Te_2O_3(OH)_2$, i.e. $Te_2O_3(OH)(NO_3)$ and $Te_2O_3(OH)(ClO_4)$ and are thus quite analogous to $Se_2O_3(OH)(SO_4H)$.

TABLE 9.—INTERPOLATED FREEZING-POINTS OF SOLUTIONS OF SELENIUM DIOXIDE AT THE COMPOSITION $n_{SeO_2}/n^f_{H_2S_2O_7} = 1{\cdot}00$

$m^f_{H_2S_2O_7}$	f.p. (°C)	θ (°C)	i
0·080	9·72	0·65	1·33
0·102	9·56	0·81	1·30
0·131	9·31	1·06	1·32
0·172	9·03	1·34	1·27
0·263	8·50	1·87	1·16

EXPERIMENTAL

Selenium dioxide. The commercial product was dissolved in AnalaR nitric acid and the solution evaporated to dryness. The selenium dioxide was then sublimed and collected as white needle-like crystals which were stored over phosphoric oxide in a desiccator.

Tellurium dioxide. The commercial product was evaporated to dryness with AnalaR nitric acid. It was then dissolved in sodium hydroxide solution and the resulting solution filtered. Tellurium dioxide was reprecipitated by addition of dilute hydrochloric acid. The product was well washed with water and dried at 300°C.

Apparatus and experimental procedure. The techniques for making the cryoscopic and conductimetric measurements have been described previously.[19,17]

[17] R. J. GILLESPIE, J. V. OUBRIDGE and C. SOLOMONS, *J. Chem. Soc.* 1804 (1957).

J. Inorg. Nucl. Chem., 1959, Vol. 9, pp. 166 to 170. Pergamon Press Ltd. Printed in Northern Ireland

THE REDUCTION OF SAMARIUM(III) TRIFLUOROACETATE WITH POTASSIUM IN LIQUID AMMONIA*

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Abstract—The reduction of samarium(III) trifluoroacetate with potassium in liquid ammonia provides evidence for only the transitory existence of Sm^{2+}. The nature of the products resulting from the reduction of this salt with one, two, and three equivalents of potassium is described. Procedures are given for the preparation of the trifluoroacetate and the corresponding 2-ammoniate.

IN earlier papers from this laboratory we have described the detection of species involving unusual oxidation states of transitional metals[1–4] by means of potentiometric titrations employing liquid ammonia solutions of potassium.[5,6] The present paper is concerned with efforts to determine whether this and/or related techniques might be applicable to the detection of lower oxidation states of the lanthanides. For this evaluation, samarium was selected because of its well known 2+ oxidation state and the possibility[7] of the 1+ state.

The selection of a suitable samarium(III) salt for use in this work was a major problem. Earlier work has shown that most simple salts of the lanthanides are either insoluble in liquid ammonia or ammonolyse either partially or completely; a noteworthy exception is the normal acetate which is slightly soluble but stable toward ammonolysis.[8] Despite the obvious complications introduced through the use of a salt involving a potentially reducible anion, samarium(III) trifluoroacetate was used because it is both soluble in ammonia and not ammonolysed at or below −33·5°.

Although these studies failed to result in the detection of any stable lower oxidation states of samarium, it seems worthwhile to record at least briefly the results of certain of the experiments.

The experiments described below show that samarium(III) trifluoroacetate reacts with successive one, two, and three molar equivalent quantities of potassium in ammonia. Although unstable brown products that are strongly indicative of the Sm^{2+} ion were observed, all of the samarium-containing products isolated contained samarium in the 3+ oxidation state; neither was there evidence for the formation of elemental samarium by either direct reduction or disproportionation. Potassium trifluoroacetate was identified as a reaction product; this suggests the formation of

* This work was supported in part by the Atomic Energy Commission, Contract AT-(40-1)-1639.
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[1] G. W. WATT, M. T. WALLING, JR. and P. I. MAYFIELD, *J. Amer. Chem. Soc.* **75**, 6175 (1953).
[2] G. W. WATT and P. I. MAYFIELD, *J. Amer. Chem. Soc.* **75**, 6178 (1953).
[3] G. W. WATT, J. L. HALL, G. R. CHOPPIN and P. S. GENTILE, *J. Amer. Chem. Soc.* **76**, 373 (1954).
[4] G. W. WATT, R. E. MCCARLEY and J. W. DAWES, *J. Amer. Chem. Soc.* **79**, 5163 (1957).
[5] G. W. WATT and J. B. OTTO, JR., *J. Electrochem. Soc.* **98**, 1 (1951).
[6] G. W. WATT and D. M. SOWARDS, *J. Electrochem. Soc.* **102**, 46, 545 (1955).
[7] H. A. EICK, N. C. BAENZIGER and L. EYRING, *J. Amer. Chem. Soc.* **78**, 5147 (1956).
[8] G. W. WATT and P. S. GENTILE, Unpublished work.

ammonobasic trifluoroacetates of samarium, but the nitrogen content of the products was incompatible with any such interpretation. While the white ammonia-insoluble products isolated were of reproducible composition, they apparently consisted of mixtures; efforts to separate these products were unsuccessful.

In independent experiments, it was established that the consumption of potassium in these reactions was not attributable to catalysed reactions with the solvent, or to the cleavage of C—F bonds. As shown below, however, reduction of the acetate ion may be involved. Thus, while ammonium trifluoroacetate reacts with potassium only to the extent of reduction of the ammonium ion, the reaction of trifluoroacetic anhydride with liquid ammonia,

$$(F_3CCO)_2O + 2NH_3 \rightarrow NH_4^+ + F_3CCO_2^- + F_3CCONH_2$$

followed by reduction with potassium consumes a total of three equivalents of potassium. Since one equivalent is consumed in the reduction of the ammonium ion and since formation of the dipotassium salt of the amide seems highly improbable, reduction of the carbonyl group is indicated. This interpretation is supported by the report by GILMAN and JONES[9] that trifluoroacetamide is reduced to the alcohol whereas the corresponding ethyl and *n*-butyl esters are stable toward reduction under the same conditions. It is noteworthy however that these experiments do not preclude the possibility of C—C bond cleavage, even though trifluoroacetic acid is stable toward strong reducing agents such as lithium aluminium hydride.[10]

EXPERIMENTAL

Materials

With the exceptions noted below, all materials used were anhydrous reagent grade chemicals.

Samarium(III) trifluoroacetate was prepared (in substantially quantitative yield), in a typical case, by the reaction between 1·61 g of samarium(III) oxide, 10 ml of trifluoroacetic acid, and 2·5 ml (25 per cent excess) of trifluoroacetic anhydride in a sealed Pyrex tube. Since the initial reaction is strongly exothermal, the tube and contents was held at room temperature for 6 hr, then heated for 24 hr at 100°. The supernatant liquid was decanted and the white residual solid was dried *in vacuo* for 8 hr at 100°. (Found: Sm, 30·4. Calc. for $Sm(C_2F_3O_2)_3$: Sm, 30·7%). That this salt is not solvolysed by liquid ammonia was demonstrated as follows; at the same time further purification was achieved and the trifluoroacetate was converted to a form suitable for use as a starting material in subsequent studies. The white solid was dissolved in anhydrous liquid ammonia at −33·5°, filtered to remove a very small quantity of white insoluble solid (presumably unreacted oxide), and the solvent was evaporated to provide the white crystalline 2-ammoniate which was dried *in vacuo* at room temperature for 2 hr. (Found: Sm, 28·1; N, 4·89; C, 13·6; H, 1·23. Calc. for $Sm(C_2F_3O_2)_3 \cdot 2NH_3$: Sm, 28·7; N, 5·35; C, 13·8; H, 1·16%).

Potassium trifluoroacetate was prepared by neutralizing trifluoroacetic acid with potassium hydroxide followed by crystallization and drying *in vacuo* at 100°, and potassium 1:1:1-trifluoroethoxide (which was once considered as a possible product of the hydrolysis of reduction reaction products) was prepared in quantitative yield

[9] H. GILMAN and R. G. JONES, *J. Amer. Chem. Soc.* **70**, 1281 (1948).
[10] A. L. HENNE, R. M. ALM and M. SMOOK, *J. Amer. Chem. Soc.* **70**, 1968 (1948).

from the reaction between potassium and the corresponding alcohol; the latter was prepared as described by HENNE *et al.*[10]

X-ray diffraction data for the four materials described above are given in Table 1.

TABLE 1.—X-RAY DIFFRACTION DATA

$Sm(C_2F_2O_2)_3$		$Sm(C_2F_3O_2)_3 \cdot 2NH_3$	
d (Å)	I/I_0	d (Å)	I/I_0
9·48	0·9	7·58	0·7
8·12	1·0	6·19	0·7
4·55	0·9	5·15	1·0
4·07	0·9	4·48	0·5[a]
2·60	0·8	4·01	0·7
2·06	0·5[a]		
$KOCH_2CF_3$		$K(C_2F_3O_2)$	
d (Å)	I/I_0	d (Å)	I/I_0
2·93	1·0	5·02	0·5
2·85	0·9	3·84	1·0
2·78	0·7	3·47	0·8
2·51	0·3	3·19	0·4
2·48	0·3	2·64	0·4
2·34	0·3	2·58	0·4[a]
1·86	0·3[a]	2·52	0·5

[a] Less intense lines not included here.

Methods

Potentiometric titrations in liquid ammonia were carried out using equipment and procedures described elsewhere.[5,6] The potassium used in these titrations was redistilled and stored in tared glass ampoules.[11] Reactions in liquid ammonia on a larger scale were carried out using equipment and procedures similar to those described by WATT and KEENAN.[12] All reactions in ammonia at both −33·5 and −70° were effected under strictly anhydrous conditions; transfers of both starting materials and reaction products were made in an anhydrous oxygen-free atmosphere.

X-ray diffraction patterns were obtained with a Hayes spectrograph using $CuK\alpha_1$ radiation, a tube voltage of 30 kV, a filament current of 15 mA, and exposure times of 4–6 hr. Magnetic susceptibility measurements were made with a modified Curie–Cheneveau balance.[13] Infra-red spectra were obtained using a Baird Model 4-55

[11] G. W. WATT and D. M. SOWARDS, *J. Amer. Chem. Soc.* **76**, 4742 (1955).
[12] G. W. WATT and C. W. KEENAN, *J. Amer. Chem. Soc.* **71**, 3833 (1949).
[13] F. W. GRAY and J. FARQUHARSON, *J. Sci. Instrum.* **9**, 1 (1932).

infra-red spectrometer; pellet samples (1 per cent in spectroscopically pure KBr) were prepared in an inert atmosphere.

Potentiometric titrations

In a typical experiment, 0·328 g (0·670 mmole) of samarium(III) trifluoroacetate and 0·111 g (2·85 mmoles) of potassium were dissolved in 24·7 and 31·0 ml of liquid ammonia, respectively; 18·8 ml of the trifluoroacetate solution was transferred to the titration cell and titrated with the potassium solution at −34°. During the early stages of the titration, the gradual increase in potential was most evident in the regions corresponding to one and two equivalents of added titrant, but these "end-points" were not convincing. For example, the increase in potential near the second equivalence point amounted to only 130 mV. When potassium in excess of two equivalents was added, a white gelatinous precipitate began to form and a major increase in potential occurred after three equivalents of potassium were added; at this point the rate of utilization of the added potassium decreased markedly. Essentially the same observations were made when the titrations were carried out at −70°, but the changes in potential corresponding to both one and two equivalents of potassium were more pronounced.

Reduction of the trifluoroacetate ion

This possibility was studied by the potentiometric titration of ammonium trifluoroacetate with potassium and the titration of an equimolar mixture of ammonium trifluoroacetate and trifluoroacetamide with potassium. Thus, 0·358 g of trifluoroacetic acid was dissolved in 33·1 ml of liquid ammonia to provide a 0·0948 molar solution of ammonium trifluoroacetate; this was titrated at −34° with 0·328 molar potassium solution. The potassium solution reacted instantaneously, hydrogen was evolved, and a sharp increase in potential amounting to 0·6 V occurred after addition of eactly one equivalent of the titrant.

Similarly, 0·458 g of trifluoroacetic anhydride was treated with 30 ml of liquid ammonia and the resulting solution was titrated at −34° with 0·418 molar potassium solution. The first significant change in potential was observed after addition of one equivalent of the potassium solution; during the addition of this quantity of titrant, hydrogen evolution was observed. Thereafter, hydrogen was not evolved, and after the addition of two more equivalents of the titrant another major change in potential was observed and the solution remained blue for several hours.

Reduction of samarium(III) *trifluoroacetate with potassium* (1:1)

In a typical experiment, 4·406 g (8·42 mmoles) of samarium(III) trifluoroacetate 2-ammoniate was dissolved in 25 ml of liquid ammonia and treated with a solution of 0·329 g (9·42 mmoles) of potassium over a period of 5 min. At the point of contact of the two solutions, a rust-brown solution and/or precipitate formed but was at once converted to a white precipitate which then dissolved to give a colourless solution. The solvent was evaporated and the solid residue was dried *in vacuo* at room temperature and without contact with the atmosphere. (Found: Sm, 27·4; N, 2·77%; N/Sm, 1·09; μ, 1·55 B.M.) Data from an X-ray diffraction pattern led to an unequivocal identification of potassium trifluoroacetate (d = 5·08, 3·81, 3·47, and 2·55 Å). Comparison of the infra-red spectrum of this product with the spectra

of samarium(III) trifluoroacetate 2-ammoniate and potassium trifluoroacetate led to the identification of both of these substances as components of the reaction product. The former exhibits a characteristic peak[14] at 7·28 μ; the latter is characterized by peaks at 12·43 and 7·99 μ.

Reduction of samarium(III) *trifluoroacetate with potassium* (1:2)

Samarium(III) trifluoroacetate 2-ammoniate (1·60 g; 3·06 mmoles) in 50 ml of ammonia was reduced with a solution containing 0·228 g (5·83 mmoles) of potassium. The observations were the same as described above; evaporation of the solvent followed by drying yielded a grey-white solid. (Found: Sm, 25·8%; μ, 2·13 B.M.). Again, potassium trifluoroacetate was identified by means of its X-ray diffraction pattern and infra-red spectrum; the latter however did not show evidence of the presence of $Sm(C_2F_3O_2)_3 \cdot 2NH_3$.

Reduction of samarium(III) *trifluoroacetate with potassium* (1:3)

In a typical experiment, 2·546 g (4·87 mmoles) of samarium(III) trifluoroacetate 2-ammoniate dissolved in 25 ml of ammonia was treated with a solution containing 0·584 g (14·95 mmoles) of potassium (i.e., K/Sm = 3·07). After digestion at −33·5° for 1 hr, the white flocculent precipitate was separated from the colourless supernatant solution by filtration and the solid product was washed six times with 20 ml portions of ammonia.

Evaporation of the solvent from the combined supernatant solution and washings provided a white solid. (Found: K, 26·2; Sm, 0·25; N, 0·43. Calcd. for $KC_2F_3O_2$: K, 25·7%). This product gave an X-ray diffraction pattern substantially identical with that given in Table 1 for potassium trifluoroacetate.

The grey-white ammonia-insoluble product was dried *in vacuo* at room temperature. (Found: Sm, 45·3; K, 17·5; N, 1·06; C, 5·39; H, 0·75%; μ, 1·95 B.M.). This material failed to give an X-ray diffraction pattern and the infra-red spectrum could not be correlated with that of any known compounds of samarium. If it is assumed that the small nitrogen content of this material is attributable to residual solvent and that the analytical values for hydrogen are correspondingly high, the analytical data are in accord with the empirical formula, $Sm_2K_3O_6C_3HF_6$. Efforts to demonstrate that this product might be a mixture involved treatment with different solvents under a variety of conditions; however, separations could not be effected. Similarly, efforts to establish the identity of these products through the study of their hydrolysis reactions led to results that were reproducible but inconclusive.

[14] For further details see: M. L. MUGA, Dissertation, The University of Texas (1957).

J. Inorg. Nucl. Chem., 1959, Vol. 9, pp. 171 to 177. Pergamon Press Ltd. Printed in Northern Ireland

RATE OF ELECTRON TRANSFER BETWEEN VANADIUM (V) AND VANADIUM (IV) BY NUCLEAR MAGNETIC RESONANCE*

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Abstract—The rate of electron exchange between vanadium (IV) and vanadium (V) in acid solutions containing chloride ion has been measured from a study of ^{51}V nuclear resonance line broadening. It is found that the rate of electron transfer is first order in vanadium (IV) and second order in vanadium (V) and that the rate constant for the exchange reaction in 6·5 F acid solutions is $k = 1{\cdot}5 \times 10^6$ l²/mole² sec. In the solutions studied the lifetimes between the electron transfer events were in the range 0·81–14·7 $\times 10^{-4}$ sec for vanadium (V), and in the range 1·0–6·7 $\times 10^{-5}$ sec for vanadium (IV).

THE rates of certain fast electron transfer reactions can sometimes be measured under steady state conditions when one of the reactants is diamagnetic and the other is paramagnetic . Thus, we have[1] previously used the nuclear resonance of ^{63}Cu in cuprous–cupric hydrochloric acid solution to obtain the rate of electron transfer between these two oxidation states of copper. Similarly, BRUCE *et al.*[2] have studied aromatic proton resonance in mixtures of N,N′-tetramethylparaphenylenediamine and N,N′-tetramethylparaphenylenediamine positive ions in order to obtain the rate of electron transfer between these two molecules. A theory for this technique has been developed in detail by MCCONNELL and BERGER .[3] The basic idea of the method is that the nuclear resonance of a molecule or ion in the diamagnetic state is interrupted by the large magnetic hyperfine field when it is converted to the paramagnetic state. The hyperfine field arises from unpaired electrons in the paramagnetic species. In this theoretical work[3] it was shown that if hyperfine splittings can be observed in the paramagnetic resonance of a solution containing a nucleus X in both a diamagnetic molecule D and in a paramagnetic molecule P, then the nuclear resonance line width of X is a direct measure of the lifetime of the diamagnetic molecule or ion.

We are attempting to make a survey of reactions whose rates can be studied by the above described technique. The purpose of the present work is to show the applicability of this method to a determination of electron exchange rates between vanadium (IV) and vanadium (V) in acid solutions containing chloride ion. The idea that this exchange process might be extremely fast came from the earlier work of TEWES *et al.*,[4] who studied the rate of exchange between vanadium (IV) and vanadium (V) in acid solution using isotopic labelling techniques. They found essentially 100 per cent exchange in separation times of the order of 1 sec.

* Sponsored by the National Science Foundation.
† Contribution No. 2358.

(1) H. M. MCCONNELL and H. E. WEAVER, JR., *J. Chem. Phys.* **25**, 307 (1956).
(2) C. R. BRUCE, R. E. NORBERG and S. I. WEISSMAN, *J. Chem. Phys.* **24**, 473 (1956).
(3) H. M. MCCONNELL and S. B. BERGER, *J. Chem. Phys.* **27**, 230 (1957).
(4) H. TEWES, J. RAMSEY and C. GARNER, *J. Amer. Chem. Soc.* **72**, 2422 (1950).

EXPERIMENTAL AND RESULTS

All reagents were CP grade and no attempt was made at further purification. Pervanadyl stock solutions were prepared by dissolving weighed amounts of ammonium metavanadate in slightly more than one equivalent of sodium hydroxide solution and then gently heating until ammonia evolution ceased. The solution of sodium vanadate was then added to acid very slowly with rapid stirring. Rapid addition gives a red precipitate of vanadium pentoxide which does not dissolve.

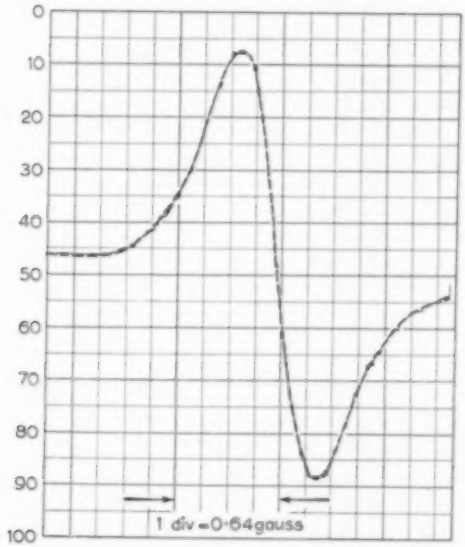

FIG. 1.—^{51}V nuclear resonance of 0·20 F vanadium (V) in solution containing 2·8 F Cl^- (as HCl), 6·50 F H^+ (as $HCl + HClO_4$).

All nuclear resonance spectra were made using a Varian wide line NMR spectrometer. Phase-sensitive detection was employed and the observed spectra are the derivatives of the absorption curve. Measurements were made at room temperature with unthermostatted samples. Resonances were observed at approximately 5·6 Mc/s and at applied fields of 5000 gauss. Representative spectra are given in Figs. 1–4. The line shapes are nearly Lorentzian; the ratios of the maximum positive slopes to the maximum negative slopes are all $4{\cdot}0 \pm 0{\cdot}2$. This line shape is required by the theory, since the theory involves the use of the Bloch equations.[3] Transverse relaxation times T_2 were obtained directly from the spectra from the peak to peak separations ΔH (in gauss):

$$1/T_2 = \sqrt{3}/2\,(\gamma\,\Delta H) \qquad (1)$$

In (1), γ is the magnetogyric ratio of vanadium; $\gamma = 7{\cdot}05 \times 10^3$ sec^{-1} gauss^{-1}. For acidic pervanadyl solutions, the transverse relaxation time T_2 is 4×10^{-4} sec. This corresponds to a peak to peak separation of 0·42 gauss. Magnetic field inhomogeneity may make an appreciable contribution to this line-width. The rate of electron exchange, however, is related to the *increase* in the $1/T_2$ relaxation frequency associated with the addition of vanadium (IV), and thus an absolute value of T_2 for pure pervanadyl solutions in a perfectly uniform field need not be known. Thus, the quantity of

experimental interest is $\delta(1/T_2)$ which is related to the increment in the peak to peak line-width due to the addition of vanadium (IV) to a solution containing a fixed amount of vanadium (V).

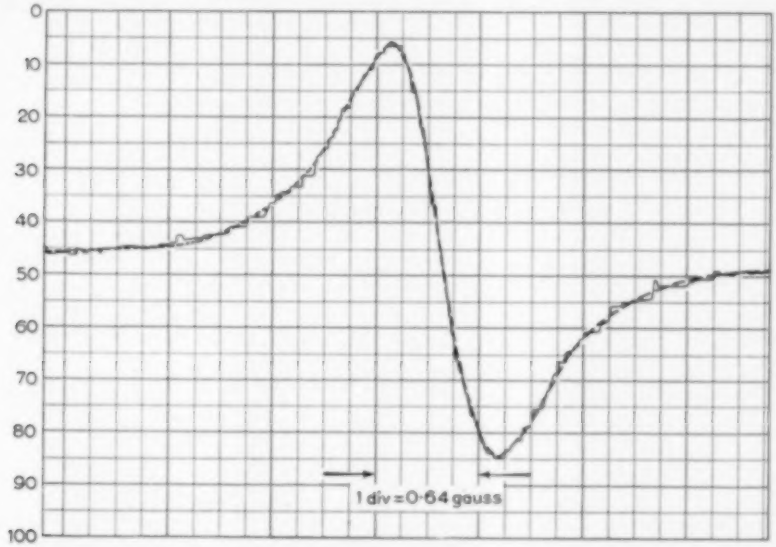

FIG. 2.—^{51}V nuclear resonance of 0·36 F vanadium (V) in a solution containing 0·10 F vanadium (IV) in 4·7 F HCl.

Experiments showed that addition of vanadium (IV) to vanadium (V) solutions in the presence of chloride but at relatively low acid concentrations had essentially no effect on the vanadium resonance line-width. See Fig. 2. It was found, however,

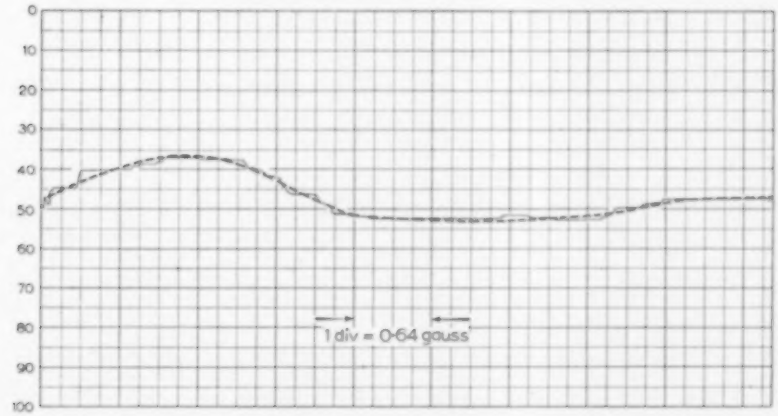

FIG. 3.—^{51}V nuclear resonance of 0·22 F vanadium (V) in a solution containing 0·06 F vanadium (IV), 2·6 F Cl^- (as HCl) and 7·5 F H^+ (as $HCl + HClO_4$).

that in solutions containing large concentrations of both hydrochloric and perchloric acids the vanadium (IV) had a strong effect on the vanadium (V) nuclear resonance line-width. A series of experiments was carried out in solutions having hydrogen ion concentrations from 6·5 to 7·2 F and chloride ion concentrations of 3 F. The

results are summarized in Fig. 5, which gives a plot of $\delta(1/T_2)$ vs. the formal concentration of vanadium (IV) for two different concentrations of vanadium (V).

In the region of acidity where this study was made, chloride ion is oxidized by vanadium (V) although the extent of this reaction is quite small in the time required to make our measurements. The rate of the chloride oxidation is strongly acid-dependent (in concentrated HCl, chlorine is rapidly evolved); hence we were limited

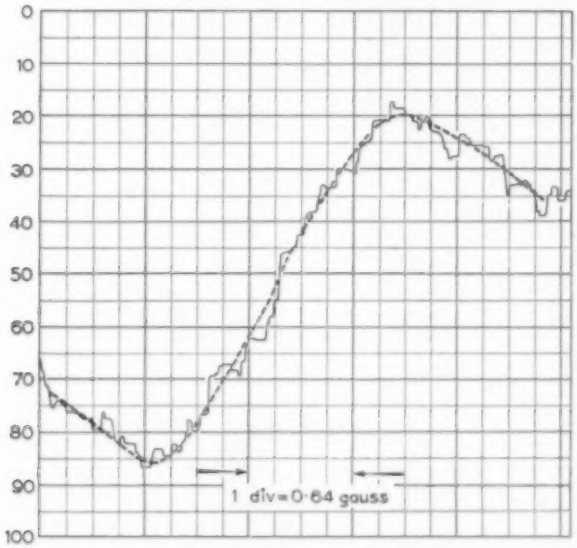

FIG. 4.—^{51}V nuclear resonance of 0·20 F vanadium (V) in a solution containing 0·025 F vanadium (IV) 2·8 F Cl^- (as HCl), and 6·50 F H^+ (as $HCl + HClO_4$).

to acid concentrations less than 8 F. Attempts to make stock solutions of vanadium (V) at these relatively high concentrations (0·4 F) in the absence of chloride ion failed. This strongly suggests that vanadium (V) is somehow complexed with chloride.

DISCUSSION

It is highly unlikely that the line broadening illustrated in Figs. 3 and 4 is due to paramagnetic dipole broadening of the vanadium (V) nuclear resonance by magnetic fields of the vanadium (IV) ions. The large effect of the hydrogen ion concentration on the vanadium (V) nuclear resonance line-width in the presence of vanadium (IV), as indicated in comparison of Figs. 2 and 3, strongly supports this data. Moreover, one would expect that if the line broadening were dipole in origin, then the vanadium (V) nuclear resonance line-width would be independent of the vanadium (V) concentration, whereas, as we shall see below, the line-width does depend on the vanadium (V) concentration. Thus, in the following discussion we attribute the line broadening of the vanadium (V) nuclear resonance to a lifetime limiting process associated with electron transfer between vanadium (V) and vanadium (IV).

According to the theory,[3] if τ_D is the lifetime of the vanadium (V) species with respect to the electron exchange reaction, then

$$1/\tau_D = \delta(1/T_2). \tag{2}$$

Necessary conditions for the validity of this equation have been discussed previously[3] and essentially involve the requirement that the paramagnetic resonance of solutions containing both vanadium (IV) and vanadium (V) show resolved vanadium hyperfine splittings. This is indeed the case, as illustrated in Fig. 7 which gives the paramagnetic resonance spectrum of the solution whose nuclear resonance is given in Fig. 4.

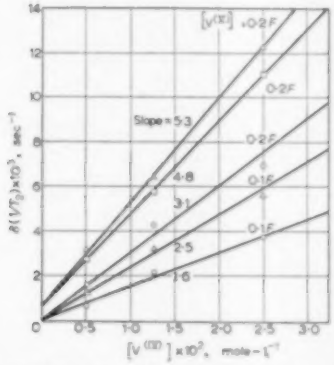

FIG. 5.—Plot of $\delta(1/T_2)$ vs. [V(IV)] for two different concentrations of vanadium (V) in solutions containing: ○ 2·8 F Cl^- (as HCl) and 6·5 F H^+ (as HCl + $HClO_4$), △ 3 F Cl^- (as HCl) and 6·7 F H^+, □ 3 F Cl^- and 7·2 F H^+.

If we write the rate of electron exchange in a solution containing (D) moles per litre of vanadium (V) and (P) moles per litre of vanadium (IV) as

$$R = k(P)^n(D)^m, \tag{3}$$

where R is the number of moles of electrons transferred per litre per seond then it

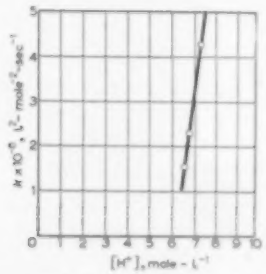

FIG. 6.—Plot of k vs. [H^+], k obtained from slopes of plots in Fig. 5.

follows that the lifetimes of vanadium (IV) and vanadium (V), τ_P and τ_D are

$$\tau_D = \frac{1}{k(P)^n(D)^{m-1}} \tag{4}$$

$$\tau_P = \frac{1}{k(P)^{n-1}(D)^m}$$

From equation (2), it follows that Fig. 5 is actually a plot of $1/\tau_D$ vs. (P). The linearity of the plots indicates that the rate of exchange is first order with respect to vanadium (IV) ($n = 1$) and values of the slopes for two different concentrations of

vanadium (V) show that $m = 2$. That is, the rate of electron transfer is second order in the vanadium (V) concentration. The number of moles per litre of electrons transferred per second in a solution containing vanadium (IV) and vanadium (V) is therefore $k(P)(D)^2$, where the value of k obtained from the plots in Fig. 5 is $k = 1{\cdot}5 \times 10^6$ l^2/mole^2 sec at 6·5 F acid concentration and 3 F chloride concentration.

It was found that the line broadening and hence the rate of the reaction was very sensitive to hydrogen ion concentration. This is illustrated in Fig. 6 where k varies directly as $[H^+]$ in the small range of acidity shown. Measurements were made at high acid (7 F) in the absence of chloride ion, and it appears that the rate of electron

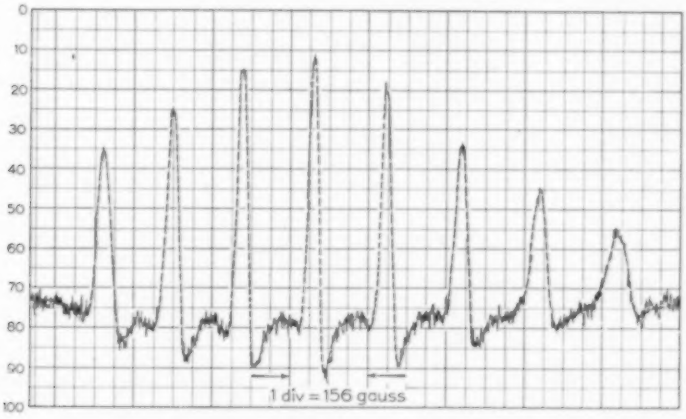

FIG. 7.—Electron paramagnetic resonance spectrum of 0·025 F vanadium (IV) in a solution containing 0·20 F vanadium (V), 2·8 F Cl^- (as HCl), and 6·50 F H^+ (as HCl + $HClO_4$). Klystron frequency is 9500 Mc/s and $g = 2{\cdot}0$.

exchange is rapid. Because of the low sensitivity, however, we did not attempt to determine the rate constant or the order with respect to vanadium (V) under these conditions. This suggests that there is a path for exchange not involving chloride, although under the conditions of our measurements the vanadium cations are almost certainly complexed to some extent by chloride ions.

EXCHANGE MECHANISM

The mechanism of this exchange reaction is by no means evident to us. If one assumes that there exists a rapid monomer–dimer equilibrium involving vanadium (V) where the monomer is the predominant species and where the dimer is much more reactive with respect to electron exchange than the monomer, one obtains a mechanism consistent with the rate equation.

$$2V(V) \rightleftarrows (V(V))_2 \tag{5}$$

$$(V(V))_2 + V(IV) \rightarrow (V(V))_2 + V(IV) \text{ (electron exchange)} \tag{6}$$

We hesitate to speculate as to why the dimer should be more reactive than the monomer with respect to this transfer.

Metal ions are known to polymerize in aqueous solution,[5-8] but all of the

[5] E. KING and M. PANDOW, *J. Amer. Chem. Soc.* **74**, 1966 (1952).
[6] F. ROSSOTTI and H. ROSSOTTI, *Acta Chem. Scand.* **10**, 957 (1956).
[7] J. HEDSTRÖM, *Arkiv För Kemi* **6**, 1 (1953–54).
[8] F. DUKE and F. PARCHEN, *J. Amer. Chem. Soc.* **73**, 2890 (1951).

work done has been carried out at relatively low acidities and thus would not apply directly to our situation. In addition, dimer and polymer formation is always favoured toward low acidities in hydrolysis type equilibria as in the case of Fe(III):[7]

$$2Fe^{3+} + 2H_2O \rightleftarrows Fe_2(OH)_2^{4+} + 2H^+ (K_{eq} = 1{\cdot}2 \times 10^{-3}) \quad (7)$$

It is conceivable however that oxygenated cations such as those formed by vanadium (IV) and (V) could act as bases as well as acids:

$$2VO_2^+ + 2H^+ \rightleftarrows V_2O_3^{4+} + H_2O \quad (8)$$

Acknowledgement—We gratefully acknowledge the stimulating discussions concerning this problem with Professor E. L. KING.

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THE SILVER CATALYSED OXIDATION OF MANGANOUS ION BY PERSULPHATE

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(*Received in final form*, 7 *June* 1958)

Abstract—THE oxidation of bivalent manganese by persulphate is very slow, but becomes fast in the presence of the silver ions. The product of oxidation is trivalent manganese which immediately disproportionates into manganese dioxide and divalent manganese. The kinetics were followed by running the reaction mixture into excess of oxalic acid and estimating the unused oxalic acid with permanganate. The reaction was found to be first order with respect to the persulphate ion and zero order with respect to the manganous ion. The salt effect is negative and exponential. The energy and entropy of activation have been calculated. The entropy is negative. In the presence of sulphuric acid the reaction mixture turns slightly red and the reaction rate appears to be much slowed down in sulphuric acid of strength 3·6 M and above. A mechanism has been suggested consistent with the observed facts.

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As early as 1901 MARSHALL,[1] and DITTRICH and HASSEL[2] reported the oxidation of manganous ion to manganese dioxide in aqueous solution by persulphate. MARSHALL[1] and STEHMAN[3] also found that the oxidation is carried to the permanganate stage in the presence of silver ions as catalyst. Ordinarily the oxidation of manganous ion by persulphate is very slow, but the silver-catalysed reaction is measurable. Generally such oxidation–reduction reactions take place in several steps, each being accompanied by one electronic change. Hence tripositive manganese is possibly formed as the first oxidation product which immediately disproportionates into manganese dioxide and bivalent manganese, especially in the absence of sufficient acid.

The kinetics of this reaction were studied by DEKKER *et al.*,[4] who found the first-order rate-constants to decrease with time. Their method of following the rate of the reaction is not free from objection. The reaction mixture was run into a dry flask and sodium chloride was added to precipitate silver as chloride which was subsequently filtered along with manganese dioxide, formed as the product. A known volume of the filtrate was then added to a known excess of ferrous sulphate solution and unused ferrous sulphate was titrated with a standard potassium permanganate solution. In this method ferrous sulphate is susceptible to atmospheric oxidation, giving higher estimated values of persulphate and secondly the whole process consists of so many operations that the accuracy is likely to suffer. In view of the above we employed a simpler method for following the kinetics. The reaction mixture is run into a known volume of oxalic acid and hydrochloric acid. Manganese dioxide dissolves in oxalic acid, itself being reduced to Mn(II) and HCl checks the reaction between persulphate and Mn(II) by precipitating silver as chloride.

[1] H. MARSHALL, *Chem. News* **83**, 76 (1901).
[2] M. DITTRICH and C. HASSEL, *Ber. Dtsch. Chem. Ges.* **284**, 1423 (1903).
[3] J. V. R. STEHMAN, *J. Amer. Chem. Soc.* **24**, 1204 (1902).
[4] A. O. DEKKER, H. A. LEVY and D. M. YOST, *J. Amer. Chem. Soc.* **59**, 2129 (1937).

Excess of oxalic acid is titrated against a standard solution of permanganate. The silver concentration used is low and so silver chloride does not interfere with the titration. Persulphate does not react with the oxalate in the presence of the inhibiting chloride ions.[5]

The reaction kinetics were followed in the presence of 0·25 M K_2SO_4 to keep the ionic strength almost constant. Potassium or sulphate ions do not appear to exert any specific ionic effect on this reaction. In view of the fact that traces of impurities greatly influence the oxidation reactions of persulphate,[6–8] the medium of the reaction was redistilled water from a quartz vessel.

EXPERIMENTAL

All the chemicals used were B.D.H. A.R. or E Merck G.R. quality and all the vessels for storing redistilled water, preparing solutions, the pipettes, measuring flasks and the reaction vessel itself, were of Jena glass. The reaction vessel was coated outside with black japan to exclude any photochemical effect.

Stock solutions of manganous sulphate, potassium sulphate, silver nitrate, potassium permanganate and oxalic acid were prepared in the usual way. Persulphate solutions were always freshly prepared by direct weighing for each set of experiments and its concentration checked by arsenite[9] or ECKARDT's[10] method.

Calculated quantities of persulphate, potassium sulphate and manganous sulphate solutions were taken in the reaction vessel and put in a thermostat at 35°C. Silver nitrate solution also was kept in the thermostat separately. The total volume of the reaction mixture was 100 ml on mixing the known amount of silver nitrate. After suitable intervals of time, 5 ml of the reaction mixture were pipetted out and estimated as already described.

RESULTS AND DISCUSSION

The reaction rate increases with the increase in the concentration of the persulphate and the reaction is first order with respect to this ion. The amount of manganese dioxide formed is independent of the concentration of the manganous sulphate. Table 1 gives the results of one experiment. The reaction is, in fact, bimolecular, but has a first order rate-constant because the concentration of the catalyst, silver ion, remains constant. The first order catalytic constants were calculated from the relation

$$k_\gamma = \frac{2{\cdot}3}{t} \times \frac{1}{C_{Ag}} \log \frac{a}{a-x} \qquad (1)$$

Persulphate concentrations were calculated from the amount of manganese dioxide estimated.

Table 2 gives a summary of the average values of the first order constants with different concentrations of persulphate and manganous sulphate. The constants quite clearly show that the reaction is apparently first order.

In order to elucidate the mechanism of this reaction, we have also carried out some experiments to determine the salt effect; the electrolytes used were, potassium, ammonium and magnesium sulphates, potassium nitrate and sodium acetate. Table 3 gives the values of the ionic strengths and the corresponding first-order rate constants.

[5] S. P. SRIVASTAVA and S. GHOSH, *Z. Physik. Chem.* **202,** 191 (1953).
[6] C. V. KING, *J. Amer. Chem. Soc.* **52,** 4779 (1930).
[7] Y. K. GUPTA and S. GHOSH, *Proc. Ind. Sci. Cong. Sec.* 4, *Abstr.* 49 (1958).
[8] T. L. ALLEN, *J. Amer. Chem. Soc.* **73,** 3589 (1951).
[9] Y. K. GUPTA and S. GHOSH, *Anal. Chim. Acta* **17,** 379 (1957).
[10] LE BLANK ECKARDT, *Chem. News* **81,** 38 (1900).

A plot of log k_γ against the ionic strength or its square root, gives almost a straight line with a negative slope in both cases. However, a better agreement between theory and experiment is found in the latter case, suggesting the reaction between oppositely

TABLE 1.—$K_2S_2O_8$ = 0·06 M, $MnSO_4$ = 0·04 M, K_2SO_4 = 0·25 M, $AgNO_3$ = 0·002 M
Temp. 35°C

Time (min)	Volume of 0·02 N $KMnO_4$ for 5 ml of reaction mixture	Concentration of MnO_2 ($\times 10^3$ N)	Concentration of $K_2S_2O_8$ ($\times 10^2$ M)	First order constants (l./mole/min)
0	5·06	—	6·000	—
10	4·79	1·08	5·946	0·448
20	4·54	2·08	5·896	0·443
30	4·27	3·16	5·842	0·449
40	3·98	4·32	5·784	0·460
50	3·72	5·36	5·732	0·455
60	3·48	6·32	5·684	0·452
70	3·18	7·84	5·624	0·463
80	2·92	8·88	5·572	0·461
90	2·64	9·68	5·516	0·466
100	2·45	10·44	5·478	0·455
110	2·26	11·20	5·440	0·445
120	2·02	12·16	5·392	0·445
130	1·80	13·04	5·348	0·443
150	1·30	15·04	5·248	0·447
160	1·02	16·16	5·192	0·450
			average	0·452

TABLE 2.—K_2SO_4 = 0·25 M, $AgNO_3$ = 0·002 M

Concentration of persulphate (M)	Concentration of manganous sulphate (M)	Ionic strength	k_γ (l./mole/min)
0·02	0·02	0·892	0·448
0·02	0·04	0·972	0·447
0·02	0·01	0·852	0·449
0·04	0·01	0·912	0·460
0·04	0·02	0·952	0·469
0·04	0·04	1·042	0·453
0·06	0·04	1·092	0·452
0·06	0·02	1·012	0·456

charged ions[11] or between an ion and a neutral molecule. The behaviour of sodium acetate is slightly different from other electrolytes, possibly due to the specific effect of the sodium ions.

It is apparent from the results in Table 4 that acetic acid and lower concentrations

[11] A. A. FROST and R. G. PEARSON, *Kinetics and Mechanism* p. 139. Wiley, New York (1953).

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of H_2SO_4 have almost no influence on the reaction rate. The titration of the reaction mixture with permanganate is difficult with higher concentrations of H_2SO_4 (3·6 N and above). In strong acid solution the reaction mixture had a tendency to turn red, forming stable trivalent manganese. The titre values of the permanganate were high, which indicated a slow rate of reaction in high concentrations of H_2SO_4. In the

TABLE 3.—$K_2S_2O_8$ = 0·06 M, $MnSO_4$ = 0·02 M, $AgNO_3$ = 0·002 M

Electrolyte	Ionic strength	k_γ(l./mole/min)
K_2SO_4	1·012	0·456
K_2SO_4	0·637	0·540
K_2SO_4	0·422	0·617
KNO_3	0·765	0·518
KNO_3	0·512	0·591
$(NH_4)_2SO_4$	1·762	0·391
$(NH_4)_2SO_4$	1·012	0·457
$MgSO_4$	0·762	0·527
CH_3COONa	0·512	0·410
CH_3COONa	0·387	0·545
CH_3COONa	0·287	0·673

TABLE 4.—$K_2S_2O_8$ = 0·06 M, $MnSO_4$ = 0·02 M, K_2SO_4 = 0·25 M, $AgNO_3$ = 0·002 M

Acid	Concentration (N)	k_γ (l./mole/min)
Acetic	0·4	0·440
Sulphuric	0·05	0·469
Sulphuric	0·10	0·467
Sulphuric	0·90	0·460
Sulphuric	1·80	0·408
Sulphuric	3·60	0·322

presence of 0·5 M potassium fluoride also, the reaction rate is much slowed down and the reaction mixture turns slightly red indicative of trivalent manganese which forms a complex with KF. The exact nature of these effects in strong sulphuric acid medium, or in the presence of KF, is under investigation.

The effect of increasing the concentration of $AgNO_3$ on the rate of this reaction is almost linear, as will be seen from Table 5 where the rate constants have been calculated from the relation

$$k = \frac{2{\cdot}3}{t} \log \frac{a}{a - x}$$

The reaction was also, studied at 40°, 45° and 50°C and Table 6 gives the average values of k_γ at these temperatures using two concentrations of persulphate, 0·06 M and 0·02 M, and one concentration of manganous sulphate, 0·02 M.

The average value of the heat of activation is 15,020 cal for the range 35°–50°C.

Using this value of heat of activation, the frequency factor and entropy of activation have been calculated at different temperatures. Mean values of the frequency factor and entropy of activation are $3{\cdot}74 \times 10^8$ sec^{-1} and $-20{\cdot}2$ E.U. respectively.

TABLE 5.—$K_2S_2O_8 = 0{\cdot}04$ M, $MnSO_4 = 0{\cdot}02$ M

Concentration of silver nitrate (M)	k_γ^1(min^{-1})
0·001	0·00847
0·002	0·01624
0·003	0·02415
0·004	0·03401

TABLE 6

Temperature (°C)	k_γ (l/mole/min)
35	0·4531
40	0·6850
45	0·9660
50	1·4359

Mechanism

The factors which decide the mechanism are the order of the reaction, salt effect and the entropy. The reaction is first order with respect to persulphate ion and zero order with respect to manganous ion. Hence the rate determining step does not involve the manganous ion. The entropy of activation is negative and hence the reaction should be either between two similarly charged ions or between a charged ion and a neutral molecule.[12] A possible mechanism involving oppositely charged ions is as follows:

$$S_2O_8^{--} \rightleftharpoons 2SO_4^- \qquad \text{rapid} \quad (1)$$

$$2SO_4^- + Ag^+ \rightarrow Ag^{3+} + 2SO_4^{--} \qquad \text{slow} \quad (2)$$

$$Ag^{3+} + 2Mn^{++} \rightarrow Ag^+ + 2Mn^{3+} \qquad \text{fast} \quad (3)$$

$$2Mn^{3+} \rightarrow Mn^{4+} + Mn^{++} \qquad \text{fast} \quad (4)$$

The rate determining step is (2)

from (2) $$-\frac{dc}{dt} = k_2[Ag^+][SO_4^-]^2$$

also from (1) $$\kappa = \frac{[SO_4^-]^2}{[S_2O_8^{--}]}$$

where κ is the equilibrium constant

Hence $$-\frac{dc}{dt} = \kappa k_2[S_2O_8^{--}][Ag^+] = k[S_2O_8^{--}]$$

[12] A. A. FROST and R. G. PEARSON, *Kinetics and Mechanism* p. 135. Wiley, New York (1953).

The experimentally measured constant k_γ is equal to $\frac{k}{[Ag^+]}$

where $k = \kappa k_2[Ag^+]$

$$\therefore \quad k_2 = \frac{k}{\kappa[Ag^+]} = \frac{k_\gamma}{\kappa} \quad (\kappa \text{ will be low, of the order of } 10^{-6})$$

$$\therefore \quad k_2 = \frac{0{\cdot}452}{\kappa} = 4{\cdot}52 \times 10^7 \text{ l./mole/min}$$

Calculation of the frequency factor and the entropy of activation of the rate determining step (2) gives the values $3{\cdot}73 \times 10^{16}$ sec^{-1} and 16·29 E.U. respectively. This indicates that the reaction is between oppositely charged ions. These calculated values do not support the generally accepted mechanism $S_2O_8^{--} + Ag^+ \rightarrow 2SO_4^{--} + Ag^{3+}$ because the observed frequency factor is too low. The calculated high frequency factor suggests that the slow reaction step is not between $S_2O_8^{--}$ and Ag^+, but between silver ion and some product of persulphate which is negatively charged.

Some visual observations were made on mixing persulphate and silver nitrate solutions. A black suspension is produced, which increases with time and is directly proportional to the concentrations of persulphate and silver ions. This indirectly supports the steps (1) and (2) of the mechanism. YOST[13] concluded, based on his experiments, that this suspension is a compound of trivalent silver whereas MALAGUTI[14] is in favour of a compound of bivalent silver.[15] Many others believe that it is a mixture of both. We also could not arrive at a decisive conclusion regarding its composition. But it is beyond doubt that this black material is some higher valent silver compound and has high oxidizing capacity. From the viewpoint of the mechanism of the reaction, the uncertainty about the higher valence of the silver is of less importance, although its investigation may be interesting in itself. Hence, in view of the above, we conclude that higher valent silver is definitely formed, either in the form of Ag^{2+} or Ag^{3+}. In our kinetic experiments no such blackening was obtained because the concentration of the silver used was low. Moreover the higher valent silver instantaneously oxidizes Mn(II) and itself reduces back to monovalent silver. The value of the first-order rate constant at 25°C (by extrapolation from the straight line obtained by plotting $\log k_\gamma$ against $1/T$) is 0·2089 which is of the same order as found by other workers for the oxidation of hydrazine,[4] ammonia,[16] cerous ion,[17] vanadyl ion,[18] acetone[19] and trivalent chromium[13] and which supports the view of the previous workers that little or no specific effect of the reducing agent is involved in each of these persulphate oxidations.

[13] D. M. YOST, *J. Amer. Chem. Soc.* **48**, 152 (1926).
[14] A. MALAGUTI, *Anal. Chim.* **42**, 138 (1952).
[15] G. T. MORGAN and F. H. BURSTALL, *J. Chem. Soc.* 2594 (1930).
[16] C. V. KING, *J. Amer. Chem. Soc.* **49**, 2689 (1927).
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[18] D. M. YOST and W. H. CLAUSSEN, *J. Amer. Chem. Soc.* **53**, 3349 (1931).
[19] E. BEKIER and S. W. KIJOWSKI, *Roczniki Chem.* **15**, 136 (1937).

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THE EFFECT OF CHOICE OF SOLVENT ON THE EXTRACTION OF COBALT(II) THIOCYANATE COMPLEXES

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(*Received* 22 *May* 1958)

Abstract—The extraction of cobalt(II) from aqueous $HClO_4$–NaNCS has been studied with a variety of ketones, alcohols, ethers and *n*-hexane. The order of increasing ability to extract cobalt(II) thiocyanates was found to be *n*-hexane, ethers, alcohols, ketones. The role of the solvent has been related to electron donor properties, steric factors and dissociation of the extracted complexes in the several solvents.

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PRELIMINARY to our study of the distribution of cobalt(II) between aqueous $HClO_4$–NaNCS and methyl *iso*butyl ketone,[1] it was necessary to examine a variety of solvents in order to select one which was suitable for the extensive examination. In the course of this preliminary survey several interesting results appeared, which caused us to extend the study of the role of the solvent in the extraction of cobalt(II) thiocyanate complexes.

As early as 1879, VOGEL[2] reported the extraction of cobalt(II) thiocyanate complexes into a 1:1 mixture of amyl acetate and amyl ether. More recently several investigators[3,4] have established the thiocyanate extraction as a standard colorimetric procedure for cobalt.

KATZIN[5] has described the factors affecting the solubility of inorganic salts in organic solvents, so the extension of our preliminary survey of solvents naturally followed the directions suggested by KATZIN's study.

EXPERIMENTAL

Materials

Perchloric acid, sodium thiocyanate, and cobalt carbonate were J. T. Baker "analysed" reagent grade chemicals. Perchloric acid stock solutions were standardized by comparison with standard, carbonate-free NaOH. Sodium thiocyanate was recrystallized from distilled water; stock solutions were made and analysed by conventional gravimetric procedures. Sodium perchlorate, from G. Frederick Smith Chemical Company, was recrystallized from distilled water, separated by filtration and dried over a portion of the salt which had been previously dried in an oven at 110 to 115°C for 48 hr. A stock solution was made and its concentration determined by evaporating a known volume of solution to dryness, heating to 160° to remove the one water of hydration, and weighing. A check showed that this method gave the same result as prolonged heating at 300°. (The analysis of this solution was the same as one prepared by neutralizing a known amount of perchloric acid with reagent sodium hydroxide, and diluting to the required volume.) Cobalt(II) perchlorate was prepared from cobalt carbonate and perchloric acid and was recrystallized twice from distilled

[1] C. E. JOHNSON and C. H. BRUBAKER, Paper in preparation.
[2] H. W. VOGEL, *Ber. Dtsch. Chem. Ges.* **12**, 2314 (1879).
[3] E. B. SANDELL and R. W. PERLICH, *Industr. Engng. Chem.* (*Anal.*) **11**, 309 (1939).
[4] R. S. YOUNG and A. J. HALL, *Industr. Engng. Chem.* **18**, 265 (1946).
[5] L. I. KATZIN, *J. Inorg. Nucl. Chem.* **4**, 187 (1957).

water. Concentrations of solutions of cobalt(II) perchlorate were checked by conventional electrolytic procedures. ^{60}Co tracer was high specific activity, processed material obtained from Oak Ridge National Laboratory as Co_2O_3. Solutions of cobalt(II) perchlorate were tagged with ^{60}Co by adding small amounts of $^{60}Co(II)$ in perchloric acid.

2:2′-dichlorodiethyl ether was obtained from the Dow Chemical Company. Methyl *iso*butyl ketone, di*iso*butyl ketone, di*iso*propyl ketone, methyl *n*-propyl ketone, methyl *iso*propyl ketone and *n*-hexanol were reagent grade Eastman Organic chemicals. Capryl alcohol, *n*-hexane-*n*-butyl ether and *cyclo*hexanone were obtained from Matheson, Coleman and Bell. Methyl *iso*amyl ketone and methyl *n*-amyl ketone were obtained from Union Carbide Chemicals. All solvents were fractionally distilled prior to use and a two degree fraction was used. Purity was indicated by the boiling point and refractive index of each.

Procedure

The solutions used in the distribution studies were prepared by adding the calculated amounts of "active" $Co(ClO_4)_2$, perchloric acid, sodium perchlorate, and sodium thiocyanate to give the appropriate initial concentrations when diluted to 25 ml with distilled water. Sodium perchlorate was used to bring the initial ionic strength to 1·50 in all cases. An equal volume of organic solvent was added to each of these solutions and each was then equilibrated in a 50 ml graduated mixing cylinder, with ground glass stopper.

The mixing cylinders were placed in a mechanical shaker in a horizontal position and were shaken overnight. Then the cylinders were hung upright in the bath until the phases separated. Four millilitre samples of each phase were placed in screw-cap vials and were counted in a well-type NaI(Tl) scintillation counter and the distribution coefficients were determined as the ratios of the counting rates in the organic and aqueous phases.

RESULTS

The results of the extraction study are given in Tables 1 and 2. It is clear that the ketones are the best for extracting the cobalt(II) thiocyanates. *cyclo*Hexanone and the unsymmetrical methyl alkyl ketones give highest values of the distribution coefficient, *D*. The two symmetrical ketones seem to extract the cobalt less well. Alcohols are also effective as reflected by the values of *D*, but we notice that the two ethers contain scarcely any cobalt (less than 0·05 per cent). As expected no extraction could be detected when *n*-hexane was used.

DISCUSSION

In his survey,[5] KATZIN has related the relative abilities of alcohols, ketones and ethers to dissolve (or extract) various metal salts and complexes (such as the cobalt(II) thiocyanates) to the electron donating abilities of such classes of solvents. The principal differences are due to the relative abilities of organic solvents to compete with anions for sites in the metal co-ordination sphere. In the case of cobalt(II), an organic liquid which can compete strongly with anions such as chloride or thiocyanate and hence tend to give six-co-ordinated ionic cobalt(II) species, does not dissolve much salt. However, if the anion competes favourably, leading to the formation of neutral, four-co-ordinate species [e.g. $H_2Co(NCS)_4$], then solubility increases. Thus, as

TABLE 1.—THE DISTRIBUTION OF Co(II) BETWEEN $HClO_4$–NaNCS SOLUTIONS IN WATER AND VARIOUS ORGANIC SOLVENTS $[Co(II)]_{init} = 0{\cdot}0400$ M; $[H^+]_{init} = 0{\cdot}500$ M; MOLAR IONIC STRENGTH = 1·50

Solvent	Distribution coefficient ($\times 10^2$)		
	$[NCS^-]_{init} = 0{\cdot}080$ M	0·160 M	0·240 M
Methyl *iso*amyl ketone	0·218	1·78	5·85
Methyl *n*-amyl ketone	0·241	1·52	5·02
Di*iso*butyl ketone	0·300	0·352	0·411
Methyl *n*-propyl ketone	8·63	37·1	98·1
Methyl *iso*propyl ketone	12·6	45·4	122
Methyl *iso*butyl ketone	0·300	4·50	15·8
Di*iso*propyl ketone*	0·327	0·468	1·48
*cyclo*Hexanone‡	118	153	26·3
n-Hexanol	2·00	3·80	5·71
Capryl alcohol*	0·203	0·673	1·75
n-Hexane	0	0	0
n-Butyl ether†	0	0	0
2:2′-Dichlorodiethyl ether*	0	0	0

* Small volume change on mixing
† Sulphur appeared at interface
‡ Organic phase volume increased by ~2 ml. Aqueous phase and organic phase exhibit same blue colour.

TABLE 2.—THE DISTRIBUTION OF Co(II) BETWEEN AQUEOUS $HClO_4$–NaNCS AND VARIOUS ORGANIC SOLVENTS $[Co(II)]_{init} = 0{\cdot}08109$ M; $[H^+]_{init} = 0{\cdot}750$ M; MOLAR IONIC STRENGTH = 1·50

Solvent	Distribution coefficient ($\times 10^2$)		
	$[NCS^-]_{init} = 0{\cdot}162$ M	0·324 M	0·487 M
Methyl *iso*butyl ketone	1·93	14·8	41·1
Di*iso*propyl ketone	0·227	1·49	4·02
n-Hexanol	5·50	10·1	15·2
Capryl alcohol	0·539	1·79	4·66
n-Butyl ether	0	0	0
2:2′-Dichlorodiethyl ether	0	0	0
n-Hexane	0	0	0

KATZIN has shown, we find ketones extract the cobalt(II) thiocyanate better than the alcohols and ethers.

The hydrocarbon, *n*-hexane, extracted no detectable amounts of cobalt, since it is completely non-polar and cannot enter into any co-ordination-solvation. Moreover, in it no dissociation of the $H_2Co(NCS)_4$ etc. can occur. It is noted[1,6] that dissociation of the complex acids has a considerable role in the extraction of the cobalt(II) thiocyanates.

Within the group of ketones a considerable difference in ability to extract cobalt(II)

[6] R. M. DIAMOND, *J. Phys. Chem.* **61**, 69 (1957).

thiocyanates is found. It does not seem possible to apply the above arguments, of electron donating ability of the several ketones, in order to explain the rather large differences observed. *cyclo*Hexanone gives the greatest amount of extraction. Next in order come the methyl alkyl ketones. The two methyl propyl ketones are distinctly better than methyl *iso*butyl ketone, which is clearly superior to the two methyl amyl ketones. The two symmetrical ketones are only about as good as the alcohols.

Such results seem to suggest that steric effects may be fairly important in the solvation of the species which do dissolve. *cyclo*Hexanone and the methyl propyl ketones may owe their superior extraction ability to their greater ability to solvate the complexes. Although the solubility order in the methyl alkyl ketones is roughly what might be predicted on the electron donating basis, *cyclo*hexanone can scarcely be so much poorer a donor than methyl amyl ketones. Indeed, if one bases electron donor strength on proton affinities,[7] methyl *iso*butyl and methyl amyl ketones should be roughly equivalent, di*iso*butyl ketone a little stronger and *cyclo*hexanone should be the best donor of this group.

Thus, in addition to (1) the competition between solvent and thiocyanate for co-ordination sites, it appears that (2) steric effects (related to solvation) and (3) simple proton affinity and dielectric constant (reflected in the ability to aid the ionization of $H_2Co(NCS)_4$ etc.) must also be considered.

If we compare the increase of D with $[NCS^-]_{init}$ in the various solvents, we notice relatively small increases in the dialkyl ketones, but rather large relative increases in the cases of the methyl alkyl etones. This seems to suggest that competition between thiocyanate and ketone is more important with the weaker bases, which are not sterically inhibited in co-ordination, but that such competition has a smaller effect with the sterically unfavourable cases or with the stronger bases (*cyclo*hexanone and the alcohols).

In the somewhat special case of *cyclo*hexanone further complications may be introduced by the higher mutual solubility with water. Further, the blue colours of the two phases suggest that both phases contain the tetrahedral cobalt(II) series.[8]

Since the two ethers have proton attracting powers of the same magnitude as the ketones,[7] it seemed strange that no extraction could be observed. However, the destruction of thiocyanate in the sulphur producing reactions between thiocyanate and the two ethers, probably accounts for this behaviour.

[7] W. Gordy and S. C. Sanford, *J. Chem. Phys.* **8**, 170 (1940).
[8] L. I. Katzin and E. Gebert, *J. Amer. Chem. Soc.* **72**, 5464, 5659 (1950).

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NOTE

The co-extraction of nitric acid and uranyl nitrate by tributyl phosphate

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As reported in a previous paper,[1] part of the nitric acid present in the aqueous phase as a salting out agent co-extracts into the organic phase during the extraction of uranyl nitrate by tributyl phosphate (TBP). Since nitric acid plays an important role in the partition of uranyl nitrate, further study has been made of the distribution of nitric acid into the organic phase in connexion with the mechanism of uranyl nitrate extraction. The extraction of uranyl nitrate alone by TBP was examined by ALCOCK *et al.*;[2] and CODDING *et al.*[3] made a chemical engineering study of uranyl nitrate and nitric acid extraction up to 6 M nitric acid concentration.

In this present study extractions were carried out, at 20° in the manner described in the earlier paper.[1] Uranium was determined gravimetrically. The nitric acid content of the organic phase could not be determined by direct titration with alkali because of precipitation of the uranium present. CARSON[4] and SHEPHERD *et al.*[5] examined methods for determination of nitric acid in presence of uranyl nitrate. The author checked these various methods and confirmed that the most satisfactory method is that of sodium oxalate complexing of the uranium. Accordingly the determination of nitric acid in the organic phase was carried out by back extraction into a constant volume of water, addition of 2% sodium oxalate solution to the aqueous backwash, and titration with 0·5 N sodium hydroxide using phenolphthalein as indicator; the value obtained was corrected by comparison with a blank test.

Aqueous phases containing 5 g uranyl nitrate per litre and varying nitric acid concentrations were extracted with 19, 39, 58 and 93% by volume TBP (water saturated) solutions in kerosene. The partition coefficients of uranyl nitrate are given in Table 1. The distribution of nitric acid during these extractions of uranyl nitrate showed a similar tendency to the results of ALCOCK *et al.*[2] for nitric acid alone.

TABLE 1.—THE PARTITION COEFFICIENT OF URANYL NITRATE AT VARIOUS TBP CONCENTRATIONS

HNO_3 conc (M) (initial aq.)	Partition coefficient			
	19%*	39%*	58%*	93%*
0·03	0·024	0·075	0·131	0·206
0·95	5·65	8·87	12·4	13·2
3·08	20·0	27·8	33·1	35·5
4·90	31·0	53·3	67·6	30·6
5·95	33·2	63·1	79·4	97·4
7·12	32·0	69·2	87·2	103
9·18	21·8	58·1	87·1	121
11·07	12·8	45·0	71·1	129
12·96	8·65	30·2	64·5	136

* This expresses the concentration (v/v) of TBP in kerosene.

[1] T. SATO, *J. Inorg. Nucl. Chem.* **6**, 334 (1958).
[2] K. ALCOCK, S. S. GRIMLEY, T. V. HEALY, J. KENNEDY and H. A. C. MCKAY, *Trans. Faraday Soc.* **52**, 39 (1956).
[3] J. W. CODDING, W. O. HAAS and F. K. HEUMANN, *Industr. Engng. Chem.* **50**, 145 (1958).
[4] W. N. CARSON, HW-29455 (1953).
[5] M. J. SHEPHERD and J. E. REIN (Editors), IDO-14316 (1955).

Further experiments were made in which aqueous phases of varying nitric acid concentration and containing 1, 5 and 10 g/l. of uranyl nitrate were extracted by 19% TBP in kerosene solution. It was observed that the uranyl nitrate partition coefficient curves for each uranyl nitrate concentration showed maxima at about 6 M nitric acid concentration, as was found for 5 g/l. uranyl nitrate

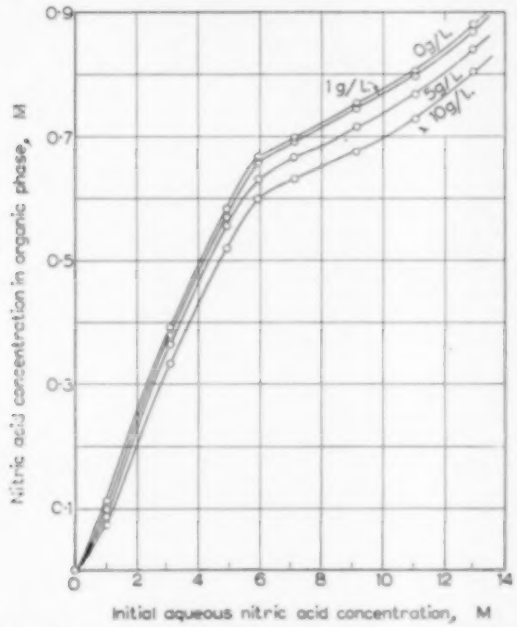

FIG. 1.—Nitric acid extraction into 19% TBP in kerosene during the extraction of aqueous uranyl nitrate of various concentrations.

in the previous paper.[1] The distribution of nitric acid during these extractions is shown in Fig. 1, in comparison with that of nitric acid alone. From Fig. 1 a correlation was made of the amounts of uranyl nitrate and nitric acid extracted into the organic phase; it was found that the extraction of nitric acid decreases linearly with increasing uranyl nitrate extraction.

TABLE 2.—EFFECT OF NITRIC ACID CONCENTRATION ON THE COMPOSITION OF ORGANIC PHASE (19% TBP IN KEROSENE)

HNO_3 conc (M) (initial aq.)	0·95	3·08	4·90	5·95	7·12	9·18	11·07	12·96
Slope of line $(HNO_3/UO_2(NO_3)_2$	1·2	2·2	2·2	2·7	2·6	3·1	3·0	3·2

As reported by HEALY *et al.*,[6] if no special reaction occurs between uranyl nitrate and nitric acid in the organic phase, it is to be expected from the formulae $UO_2(NO_3)_2 . 2$ TBP and $HNO_3 .$ TBP that one molecule of uranyl nitrate will displace two molecules of nitric acid under suitable conditions: they showed this relationship to hold in the organic phases in equilibrium with aqueous phases 6 M in nitric acid containing varying amounts of uranyl nitrate. Accordingly, the slope of each straight line correlating the concentrations of uranyl nitrate and nitric acid extracted into the organic phase was determined in order to investigate this further. The results are given in Table 2.

[6] T. V. HEALY and H. A. C. MCKAY, *Trans. Faraday Soc.* **52**, 633 (1956).

From Table 2 it is evident that although two molecules of nitric acid in the organic phase are displaced by one molecule of uranyl nitrate extracted from aqueous phases at acidities 3–9 M, this relationship does not hold at higher or lower acidities.

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DETERMINATION OF (d, α) REACTION CROSS-SECTIONS*

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Abstract—Absolute cross-sections were determined for several (d, α) reactions. Thin targets were bombarded by a beam of 7·8 MeV deuterons which were collected in a Faraday cup and measured by a current integrator. Product nuclei were separated chemically from extraneous activities. Absolute disintegration rates were determined by 4π β-counting. Cross-section values and estimated standard deviations are reported for formation of the following nuclei: ^{22}Na, ^{24}Na, ^{32}P, ^{46}Sc, 68 min ^{104}Ag, ^{113}Ag and ^{111}Ag.

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WHILE many relative cross-section values have been reported in the literature, few absolute cross-sections have been measured.[1,2] In particular reactions which are characterized by small cross-sections, such as the (d, α), have not been the subject of a systematic study.[3] Since measurable yields of the (d, α) reaction for elements of Z up to about 60 can be obtained with the high currents of 7·8 MeV deuterons of the University of Michigan cyclotron, this reaction was chosen for a detailed study. Furthermore, modern 4π β-counting techniques[4] eliminated the uncertainty in counting the product nuclei thereby permitting the determination of cross-section values of higher accuracy than had been hitherto possible. One such absolute value at a well-defined energy permits normalization of relatively precise excitation functions obtained elsewhere. For example, several excitation functions for the ^{24}Mg$(d, \alpha)^{22}$Na reaction have been reported but absolute values for a given energy vary from 180 ± 27, or 147, to 9 ± 3 mbarns. A value of 151 mbarns, good to within ± 4 per cent, as determined in this work, establishes an absolute scale for these precise relative stacked foil values.

EXPERIMENTAL[5]

A. Bombardment arrangement

The 42 in. University of Michigan cyclotron provides 7·8 MeV deuterons with deflected external beam currents as high as 100 μA. This deflected beam is magnetically focused and is collimated several times before striking the target which is placed just beyond the focal plane. The transmitted beam is caught in a Faraday cup placed behind the target. The cup is a brass cylinder, $11\frac{1}{4}$ in. long

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[1] O. U. ANDERS and W. W. MEINKE. Document number 4999, American Documentation Institute, Library of Congress, Washington, D.C. (Revised June, 1956).

[2] N. JARMIE and J. D. SEAGRAVE, Los Alamos Scientific Laboratory Unclassified Report LA-2014 (March 1956).

[3] J. P. BLASER, F. BOEHM, P. MARMIER and P. SCHERRER, *Helv. Phys. Acta* **24**, 441 (1951).

[4] B. D. PATE and L. YAFFE, *Canad. J. Chem.* **33**, 610 (1955).

[5] The apparatus and procedures outlined in this section and the experimental results given later are described in considerably more detail in the Ph.D thesis of K. L. HALL, University of Michigan, 1955, and *AECU*-3126 (September 1955).

by 2½ in. inside diameter and stands on Teflon supports. The target might have been placed inside rather than in front of the cup, but this would have complicated target handling. PANOFSKY and PHILLIPS[6] found no difference between the two arrangements.

Secondary electrons produced when the beam is stopped in the cup must be prevented from escaping. Similarly, electrons produced when the deuteron beam strikes the target must be prevented from entering the Faraday cup. To accomplish this a negative suppressing potential of at least 200 V was applied to an insulated brass ring mounted in front of the cup.

B. Beam measurement

The current collected by the Faraday cup was integrated with a modified form of WATTS' integrator circuit.[7] The output powered a digital counter which gave a record of the time variation of the beam. The integrator was calibrated by feeding in a known current from a high voltage power supply and observing the counting rate with the input condenser shorted out. The difference between

TABLE 1.—DATA ON CYCLOTRON TARGETS

	Mg	S	Ti	Cd
Melting point (°C)	651	113	1800	321
Boiling point (°C)	1110	445	3000	767
Purity (%)	"High purity"	99·98	99·99	"Spec-Pure"
Supplier	Dow	Stauffer	Foote	Johnson-Matthey
Preparation method	Evaporated	Poured	Foil	Evaporated
Substrate	Mylar	Polystyrene	—	Aluminium
Thickness (mg/cm²)	0·5–1·1	2·9	29	1·9

this (maximum) current and the average value when the condenser was in the circuit was less than 0·5 per cent. The connecting cable and Faraday cup were included in the calibration. Calibration constants were 39 ± 4 and 9·9 ± 0·1 counts/min/μA for two input condensers. These values did not change during the two month period of bombardment work. Day to day variations were accounted for by secondary calibrations.

The deuteron energy has been measured by BACH,[8] the results of two separate measurements being 7·89 and 7·74 MeV. At 7·8 MeV the focusing magnet dispersion was 6·5 keV/mm. The ½ in. collimating slit placed just before the focal plane gave an energy spread of 83 keV for a point source, although the actual spread was greater because of the finite source slit at the deflector. The beam energy was degraded by about 0·08, 0·21, 1·6, and 0·08 MeV respectively in passing through the magnesium, sulphur, titanium, and cadmium targets.

C. Target preparation

The targets were supported on thin plastic substrates placed over a 2½ in. diameter hole in an aluminium frame. Usually the area covered by the target matched the hole so that deuterons striking the target would not be stopped in the frame. This procedure prevented interference due to (n, p) reactions caused by secondary neutrons.

Pertinent data for the various targets used are presented in Table 1. Thin magnesium and cadmium targets were evaporated onto their substrates in a high-vacuum metal evaporator. Sulphur targets were prepared by pouring sulphur vapour onto the polystyrene substrate.[9] A second layer of polystyrene was sealed over the target to prevent the sulphur from evaporating when struck by the deuteron beam. Titanium was used as the 0·0026 in. commercial foil.

The uniformity of the thin targets was established by determining the weight and area of several

[6] W. K. H. PANOFSKY and R. PHILLIPS, *Phys. Rev.* **74**, 1732 (1948).
[7] R. J. WATTS, *Rev. Sci. Instrum.* **22**, 356 (1951).
[8] D. R. BACH, Ph.D. Thesis, University of Michigan (1955).
[9] E. NIELSEN and A. WEINSTEIN, Brookhaven National Laboratory Unclassified Report BNL-259 (S-19) (September 1953).

pieces cut from a typical target. In the evaporated targets no variation was observed within the limits of detection (0·4 per cent standard deviation). The poured sulphur targets showed a variation of less than 2·2 per cent. The titanium foils were uniform to within about 5 per cent when measured with a micrometer.

D. Chemical separations

For the most part the (d, α) reaction products were chemically separated from other activities without addition of an inert carrier. The purpose of such carrier-free separations was to eliminate self-absorption in the absolute β-counting. For the same reason, care was exercised to prevent contamination of the sample with inert material.

The chemical yield was determined by adding a known amount of a long-lived tracer isotopic with the (d, α) product. After the short-lived components had decayed, the tracer activity was measured and the chemical yield calculated. Two bombardments were necessary to determine absolute cross-sections when the tracer isotope was also a product of the reaction studied. For the first bombardment no tracer was added and the yield of the tracer isotope was measured relative to some other (d, α) activity produced. The tracer was then added in the second bombardment and the amount of tracer recovered in the chemical procedure was calculated, the amount produced by the nuclear reaction being known.

The target substrate was always dissolved and processed with the target element. This was essential because some product nuclei were recoiled beyond the target foil. It was experimentally determined that at least 0·0005 in. of a plastic substrate was needed to catch all the recoils; in practice 0·001 in. was used. A further experiment in which a thin (~100 μg/cm^2) target of cadmium metal mounted on thin (~65 μg/cm^2) Zapon with 0·00025 in. Mylar films in front and back was bombarded with the 7·8 MeV deuterons showed no detectable backward recoil and hence recoil catcher films have been used only behind the target[10] in the following bombardments.

E. Absolute β-counting

The disintegration rate of the samples were determined by 4π counting methods. The advantages of this technique for absolute measurements have been described by several authors.[4,11–14] Problems of decay scheme, particle scattering, secondary radiation, and self-absorption are largely eliminated. With this technique, β-rays can be counted absolutely to within about 1 per cent provided the electrical field of the counter and the counting circuit are properly adjusted. Only in the case of electron capture branching[15] or delayed states with lifetimes comparable to the resolving time of the counter are there any major discrepancies between the counting rate and disintegration rate. With a 250 cm^3 chamber, samples as low as 10 disintegrations/min can be assayed.

In this work absolute decay curves of samples containing several isotopes were obtained directly with a Borkowski type[16] 4π counter. Methane was the counting gas used. The counters were operated in the proportional region (about 4500 V for pure methane) so that high counting rates could be measured without large coincidence losses. The dead time, measured by following the decay of ^{116}In over 13 half-lives, was 7·9 μsec (a correction of 1·3 per cent at 100,000 c/m). The 4π chamber was placed in a copper box for electrical shielding to reduce the input capacitance and hence the resolving time and the attenuation of pulses entering the amplifier. When 2 in. of lead surrounded the copper box, the background of the counter was about 100 counts/min.

Samples were prepared on thin Zapon films whose thickness was determined by the absorption of ^{63}Ni β-rays.[17] The radioactive deposit was usually covered with another layer of film to prevent contaminating the counter.

Film absorption corrections may be required if a significant fraction of the electrons from the low energy portion of the β-ray spectrum are absorbed in the Zapon film. While several methods

[10] S. C. Fung, Ph.D. Thesis UCRL-1465 (1951).
[11] F. G. Houtermans, L. Meyer-Schützmeister and D. H. Vincent, *Z. Physik* **134**, 1 (1952).
[12] L. Meyer-Schützmeister and D. H. Vincent, *Z. Physik* **134**, 9 (1952).
[13] R. Cohen, *Ann. Physik* (12*th series*) **7**, 185 (1952).
[14] J. L. Putman, *Brit. J. Radiol.* **23**, 46 (1950).
[15] M. H. MacGregor, Ph.D. Thesis, University of Michigan (1953).
[16] C. J. Borkowski and T. H. Handley, *ORNL*-1056 (1951).
[17] B. D. Pate and L. Yaffe, *Canad. J. Chem.* **33**, 15 (1955).

for making these corrections have been reported[11–13,15,18–22] the extrapolation method[21] was adopted for use here. The counting rates of samples on films of varying thicknesses, made from multiple Zapon layers, were extrapolated to zero thickness. This involved extrapolation over a thickness of about 15 $\mu g/cm^2$ corresponding to a range of about 2 keV electrons.[23] The samples were counted several times during decay to detect changes in film absorption as different components decayed.

Even in carrier-free separations, self-absorption may be significant due to inactive foreign material entrained in the active deposit. A lower tolerance limit for such material was experimentally determined to be ~0·5 μg of material for 0·3 MeV β-rays.

When a non-conducting plastic film is used as the source mount, a small field-free space will exist at the centre of the chamber and very weak β-rays may not escape this region to produce a pulse. This situation may be remedied by applying a thin metallic conducting layer to the film, or by reducing the aperture in the aluminium sample plate to a size where the effect is negligible. MANN and SELIGER[24] found that a low-field correction is necessary for the 0·3 MeV ^{60}Co β-ray but not for the 1·7 MeV ^{32}P β-ray when an 0·8 in. aperture is used. BORKOWSKI[16] reported that no conducting coating is necessary if the aperture is 0·5 in. or less in diameter. In this work, a 0·5 in. diameter aperture was used, and excellent agreement was obtained with the National Bureau of Standards' standardization of ^{32}P. When the existence of a voltage plateau was taken as a criterion[4] of proper functioning, the counter used here was found to work equally well with or without a gold coating for the isotopes measured. Therefore, no conducting layer was used for routine 4π counting.

Discrimination curves[18] were obtained for three voltages and three gains each time the absolute β-activity was determined. This was repeated as the sample decayed and the radiations changed in the isotopic mixture. The slope was usually zero over the flat portion of the discrimination curves.

RESULTS

A. Magnesium bombardments

Only the 2·60 year ^{22}Na and 14·93 hr ^{24}Na were observed as (d, α) products of magnesium. To determine the chemical yield, ^{22}Na tracer was added when the target was dissolved. Sodium was separated carrier-free by dissolving in a sulphuric acid–hydrogen peroxide mixture, fuming of the large excess of acid, neutralizing the remaining acid with magnesium, and adsorbing[25,26] the solution on Dowex-50 ion exchange resin in the H^+ form (obtained from Bio-Rad Laboratories, Berkeley, California). The sodium was eluted with 0·5 N HCl, and the eluant fractions were concentrated and transferred to the source mount for counting.[5]

There was no evidence of a slope in the plateau region of the discrimination curves of either ^{22}Na or ^{24}Na. The film absorption curves are also flat. The magnitude of the aliquoting error was shown to be about 2 per cent. The decay curve was resolved by least squares analysis.

Absolute cross-sections based on a single determination were:

$$\sigma(^{22}\text{Na}) = 151 \pm 6 \text{ mbarns at } 7{\cdot}8 \pm 0{\cdot}1 \text{ MeV},$$

$$\sigma(^{24}\text{Na}) = 94 \pm 4 \text{ mbarns at } 7{\cdot}8 \pm 0{\cdot}1 \text{ MeV}.$$

[18] H. H. SELIGER and L. CAVALLO, *J. Res. Nat. Bur. Stand.* **47**, 41 (1951).
[19] W. B. MANN and H. H. SELIGER, *J. Res. Nat. Bur. Stand.* **50**, 197 (1953).
[20] R. C. HAWKINGS, W. F. MERRITT and J. H. CRAVEN, *Recent Developments and Techniques in the Maintenance of Standards.* Proceedings of a Symposium held at the National Physical Laboratory (May 1951).
[21] D. B. SMITH, *AERE/I/R*-1210 (1953).
[22] G. A. SAWYER, Ph.D. Thesis, University of Michigan (1950).
[23] R. O. LANE and D. J. ZAFFARANO, *Phys. Rev.* **94**, 960 (1954).
[24] W. B. MANN and H. H. SELIGER, *J. Res. Nat. Bur. Stand.* **50**, 197 (1953).
[25] J. BEUKENKAMP and W. RIEMAN, III, *Analyt. Chem.* **22**, 582 (1950).
[26] V. J. LINNEBOM, *J. Chem. Phys.* **20**, 1657 (1952).

The errors quoted are estimated standard deviations based on a consideration of the errors of each of the component measurements.[5] The ^{22}Na cross-section includes a correction for electron capture branching. This was based on an 8 per cent branching[27–29] and a 5 per cent electron capture counting efficiency giving an overall efficiency of 96 per cent for ^{22}Na. This value has been experimentally determined by SHERR and MILLER[28] for the BORKOWSKI 4π counter.

The above cross-section values agree closely with the 147 and 92 mbarn values reported by IRVINE and CLARKE.[30] BARTELL and SOFTKY[31] obtained 9 ± 3 mbarns for the ^{22}Na yield. Russian workers found the ^{22}Na cross-section to be 180 ± 27 mbarns.[32]

B. Sulphur bombardments

The 14·3 day ^{32}P was the only (d, α) product observed in the sulphur bombardments. This was isolated carrier-free by dissolving the polystyrene substrate in a sulphuric acid–hydrogen peroxide mixture, oxidizing the sulphur with a bromine–carbon tetrachloride mixture, neutralizing with sodium carbonate and chromatographing the resulting solution by a procedure of McISAAC and VOIGT.[33] The phosphorus was adsorbed on a column of Dowex-50 ion exchange resin upon which iron hydroxide had previously been precipitated. The activity was eluted with 0·125 N NaOH and the effluent was channeled directly through a second column of Dowex-50 resin in the hydrogen form to remove sodium ion.

The chemical yield was determined by adding 24·4 day ^{33}P in the dissolution step. Since the half-lives of ^{32}P and ^{33}P differ by a factor of only 1·7, the composite decay curves were analysed by a method outlined by WORTHING and GEFFNER[34] and applied by BILLER[35] and more recently by others[36,37] to decay curve resolution. In this method, the gross decay curve is written as a sum of two exponentials and rearranged to give

$$Ae^{\lambda_2 t} = A_1^0 \exp(\lambda_2 - \lambda_1)t + A_2^0.$$

The left member is plotted against the exponential, and the slope and intercept give the initial activity of each component. In this way resolution into ~2000 and ~10,000 counts/min of ^{33}P and ^{32}P was accomplished. Discrimination and film absorption curves were flat for the ^{32}P samples.

The cross-section based on a single determination was found to be

$$\sigma(^{32}\text{P}) = 300 \pm 200 \text{ mbarns at } 7{\cdot}7 + 0{\cdot}1 \text{ MeV}.$$

The error quoted is a rough estimate of the standard deviation, and is large because

[27] W. F. HORNYAK and T. COOR, *Phys. Rev.* **92**, 675 (1953).
[28] R. SHERR and R. H. MILLER, *Phys. Rev.* **93**, 1076 (1954).
[29] G. CHARPAK, *J. Phys. Radium* **16**, 62 (1955).
[30] J. W. IRVINE, JR. and E. T. CLARKE *J. Chem. Phys.* **16**, 686 (1948).
[31] F. O. BARTELL and S. SOFTKY, *Phys. Rev.* **84**, 463 (1951).
[32] N. A. VLASOV, S. P. KALININ, A. A. OGLOBLIN, V. M. PANKRAMOV, V. P. RUDAKOV, I. N. SERIKOV and V. A SIDOROV, *Soviet J. Atomic Energy* **2**, 169 (1957).
[33] L. D. McISAAC and A. VOIGT, Iowa State College Unclassified Report *ISC*-271 (1952).
[34] A. G. WORTHING and J. GEFFNER, *Treatment of Experimental Data* Chap. 2. John Wiley, New York (1943).
[35] W. F. BILLER, Ph.D. Thesis, *UCRL*-2067 (1952).
[36] E. C. FREILING and L. R. BUNNEY, *Nucleonics* **14**, No. 9, 112 (1956).
[37] D. H. PERKEL, *Nucleonics* **15**, No. 6, 103 (1957).

of several unknown errors, such as loss of sulphur during bombardment, volatilization during the sulphuric acid treatment, and variations in target thickness.

C. Titanium bombardments

Four (d, α) activities were produced when titanium was bombarded. Three have similar half-lives; ^{44}Sc, ^{47}Sc, ^{48}Sc with 2·4 day, 3·44 day, and 1·83 day half-lives, respectively, while the half-life of ^{46}Sc is 85 days. The latter was the isotope used in the chemical yield measurement. The titanium targets were dissolved in a sulphuric acid–hydrogen peroxide mixture and then treated with nitric acid. The scandium was separated carrier-free as a radiocolloid[38–40] by neutralizing with ammonium hydroxide to pH 8·5, adsorbing the resultant colloidal scandium on Whatman No. 50 filter paper while keeping the titanium in solution with excess hydrogen peroxide, and finally dissolving the adsorbed scandium with hydrochloric acid. Three cycles gave adequate decontamination from extraneous activities.

Discrimination curves exhibited a flat plateau but film absorption was not negligible. The decay curve was resolved into two components, the 85 day ^{46}Sc and a 2·8 day composite ^{44,47,48}Sc. Tracer ^{46}Sc, used in measuring the chemical yield, was referred to the composite 2·8 day activity. Two determinations gave cross-sections of 0·18 and 0·70 mbarns. As there was no reason to reject either, they were averaged to give:

$$\sigma(^{46}\text{Sc}) = 0{\cdot}44 \pm 0{\cdot}37 \text{ mbarn at } 7{\cdot}0 \pm 0{\cdot}8 \text{ MeV}$$

D. Cadmium bombardments

Four (d, α) products were identified in the silver fraction from cadmium bombardments. These were the 27 min and 68 min ^{104}Ag isomers, the 7·6 day ^{111}Ag, and the 3·2 hr ^{112}Ag. The silver was separated by dissolving the target in nitric acid, adding silver carrier, precipitating silver chloride, dissolving in ammonium hydroxide, scavenging with iron hydroxide and repeating this cycle three times. The chemical yield was determined gravimetrically.

The discrimination curves were flat. The cross-sections for three silver isotopes based on a single determination were found to be

$$\sigma(68 \text{ min } ^{104}\text{Ag}) = 1{\cdot}7 \pm 0{\cdot}2 \text{ mbarn at } 7{\cdot}8 \pm 0{\cdot}1 \text{ MeV}$$

$$\sigma(^{112}\text{Ag}) = 0{\cdot}49 \pm 0{\cdot}02 \text{ mbarn at } 7{\cdot}8 \pm 0{\cdot}1 \text{ MeV}$$

$$\sigma(^{111}\text{Ag}) = 0{\cdot}40 \pm 0{\cdot}04 \text{ mbarn at } 7{\cdot}8 \pm 0{\cdot}1 \text{ MeV}.$$

The errors are estimated standard deviations based upon consideration of the individual errors in each of the factors, but the unknown self-absorption error was not included.

DISCUSSION

The cross-sections for deuterons of energy E are summarized in Table 2 together with the approximate reaction energy, Q, and approximate coulomb barriers of the target to deuterons (V_1) and of the product to α-particles (V_2). The low cross-section for the cadmium reactions reflects the high coulomb barriers relative to the energy

[38] J. R. HASKINS, J. E. DUVAL, L. S. CHANG and J. D. KURBATOV, *Phys. Rev.* **88**, 876 (1952).
[39] J. E. DUVAL and M. H. KURBATOV, *J. Amer. Chem. Soc.* **75**, 2246 (1953).
[40] I. D. GILE, W. M. GARRISON and J. G. HAMILTON, *J. Chem. Phys.* **18**, 1685 (1950).

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of the incident particle. This bombardment energy exceeds the barrier for the other reactions listed. Unfortunately only very general trends are apparent from this table. The titanium cross-section appears to be quite low although there is no reason to disregard the value.

TABLE 2

Reaction	E (MeV)	σ (mbarns)	Q (MeV)	V_1 (MeV)	V_2 (MeV)
$^{24}Mg^{*}(d, \alpha)^{22}Na$	7·8 ± 0·1	94 ± 4	2·0	3·0	5·2
$^{26}Mg(d, \alpha)^{24}Na$	7·8 ± 0·1	151 ± 6	2·9	3·0	5·1
$^{34}S(d, \alpha)^{32}P$	7·7 ± 0·1	300 ± 200	5·0	3·7	6·6
$^{48}Ti^{*}(d, \alpha)^{46}Sc$	7·0 ± 0·8	0·44 ± 0·33	4·3	4·7	9·1
$^{106}Cd(d, \alpha)^{104}Ag$	7·8 ± 0·1	1·7 ± 0·2	8·8	8·3	15·6
$^{113}Cd^{*}(d, \alpha)^{111}Ag$	7·8 ± 0·1	0·40 ± 0·04	9·8	8·2	15·3
$^{114}Cd(d, \alpha)^{112}Ag$	7·8 ± 0·1	0·49 ± 0·02	7·5	8·2	15·3

* Possible $(d, \alpha\, n)$ contribution

Contributions to the (d, α) product yield from $(d, \alpha\, n)$ reactions are possible in the cases of ^{22}Na, ^{46}Sc and ^{111}Ag; Q values for the $(d, \alpha\, n)$ reactions are −5·4, −3·9 and 0·9 MeV, respectively. The $(d, \alpha\, n)$ products ^{33}P and ^{113}Ag were not detected experimentally in sulphur and cadmium bombardments and upper limits to the cross-section ratio for $(d, \alpha\, n)$ to (d, α) reactions were set at 0·1 and 0·05 respectively for these two elements. SCHOTT and MEINKE[41] similarly report the absence of $(d, \alpha\, n)$ reactions in zirconium at this energy. Considering finally the relative abundances of target isotopes for ^{22}Na, ^{46}Sc, and ^{111}Ag, it is felt that contribution of the $(d, \alpha\, n)$ reaction is probably minor.

Interference of $(d, \alpha\, 2n)$, $(d, d\, p\, n)$, $(d, 2p2n)$ and $(d, 2d)$ with the reaction studied can be ruled out on the basis of insufficient deuteron energy to overcome the strongly negative Q values.

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[41] G. L. SCHOTT and W. W. MEINKE, *Phys. Rev.* **89**, 1156 (1953).

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THE PREPARATION OF HIGH-PURITY PLUTONIUM METAL

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Abstract—High purity α-phase plutonium metal was produced by a process which consisted of two successive peroxide precipitations, direct hydro-fluorination with gaseous hydrogen fluoride, and reduction to metal with calcium and iodine "booster". The total detectable impurities in the metal produced varied from 94 to 276 p.p.m.

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IN the early phases of plutonium research, metallurgical measurements were of necessity made with metal which was known to be impure. As a consequence, the data from these determinations were not completely reliable. A supply of high-purity plutonium metal was therefore needed as part of the metallurgical research programme of the Los Alamos Scientific Laboratory.[1] Of the various methods considered for the preparation of high-purity plutonium metal, the bomb reduction procedure seemed to offer the greatest promise for producing metal of the quality and quantity needed. This was especially true in view of the work being done by the Laboratory at the time on high-purity calcium metal and high-purity calcia reduction crucibles.[2]

Initial purification of the plutonium was obtained by two successive peroxide precipitations with special attention directed toward the reagents and equipment used. Further purification was effected during conversion of the plutonium peroxide to plutonium tetrafluoride by direct hydrofluorination at 650°C. The thermal bomb reduction, as employed in this procedure, involved a rapid exothermic reaction between plutinoum tetrafluoride, calcium and iodine at an elevated temperature. The calcium iodide and the calcium fluoride formed a calcium fluoride–calcium iodide slag which melts at a lower temperature than calcium fluoride. The reduction reaction was initiated by rapidly heating a steel bomb containing a calcia crucible charged with the reactants. A sudden increase in the temperature of the bomb indicated that reaction had occurred. Metal produced in this manner was in the form of a regulus.

EXPERIMENTAL

Precipitation

Solutions for the first precipitation of plutonium peroxide were prepared from two sources: (1) α-phase plutonium metal dissolved in hydrochloric acid and (2) plutonium nitrate solutions. These solutions were diluted with sufficient sulphuric acid and water to give stock solutions of the following composition:

$$Pu = 0{\cdot}4\ M$$
$$H^+ = 1{\cdot}5\ M$$
$$Cl^- \text{ or } NO_3^- = 1{\cdot}6\ M$$
$$SO_4^- = 0{\cdot}15\ M.$$

[1] E. R. JETTE, *J. Chem. Phys.* **23**, 365 (1955).
[2] S. P. STODDARD and W. T. HARPER, *Amer. Ceram. Soc. Bull.* **36**, 105 (1957).

After an initial peroxide precipitation, the solid filter cake which served as feed for the second peroxide precipitation was dissolved in hot nitric acid and diluted with sulphuric acid to give a stock solution. Undissolved particles were removed by filtering the stock solutions through fine fritted glass. Nitric, hydrochloric, and sulphuric acids were made spectrochemically pure by distillation. Water was purified

TABLE 1.—ANALYSES OF INTERMEDIATES, REAGENTS AND PRODUCTS BUTTON NUMBER 10*

Element	First peroxide precipitate	Second peroxide precipitate	PuF_4	Ca	CaO crucible	Metal top	Metal bottom	Metal core
Li	<0·2	<0·2	<0·2	<0·2	<0·2	<0·2	<0·2	<0·2
Be	<0·2	<0·2	<0·2	<0·2	<0·2	<0·2	<0·2	<0·2
Na	140	135	<100	<5	<5	<5	<5	<5
Mg	40	<3	40	3	300	<3	<3	<3
Ca	>10⁴	15				20	20	30
Al	<10	8	20	2	1000	<5	10	10
La	1000	15				<10	<10	<10
Si	40	90	30	2	1000	15	7	7
Pb	750	<1	7	<1	<1	30	<1	<1
Cu	5	<1	2	2	4	5	3	<1
Ni	100	45	75	<2	20	10	7	5
Cr	<5	<5	<5	<5	5	<5	<5	<5
B†	0·6	0·7	0·4	<1	2	<0·5	<0·5	<0·5
Mn	<3	7	<3	20	6	30	25	30
Sn	10	6	2	<1	<1	<1	1	3
Bi	<1	60	75		<1	<1	<1	<1
Fe†	180	135	120	1	800	<30	<20	<20
V	<20	<20	<20	<20	<20	<20	<20	<20
Cd	<1	<1	<1	<1	<1	<1	<1	<1
Co	<10	<10	<10	<10	<10	<10	<10	<10
Ba	<10	<10	<10			<10	<10	<10
Mo	<20	<20	<20			<20	<20	<20
Hg	<3	<3	<3			<3	<3	<3
Sb	<10	<10	<10			<10	<10	<10
Ag	<1	<1	<1	<1	<1	<1	<1	<1
As	<20	<20	<20	<20	<20	<20	<20	<20
In	<1	<1	<1	<1	<1	<1	<1	<1
Zn	500	30	20		<30	<30	<20	<20
C†				20	100	25	20	20
S†		1·72%	0·18%	<25		30	<10	<10

* Figures are expressed in p.p.m. except as noted.
† Analysis by other than spectrochemical method.
Yield = 96·3 per cent by weight.

by deionization followed by distillation from an alkaline permanganate solution through a three stage Snyder column. The purity of this water was $\leqslant 1$ p.p.m. (as NaCl) when measured on a Branstead Model PM-2 conductivity meter.

The plutonium peroxide precipitation was performed by the procedure described by LEARY *et al.*[3] To 1 l. of stock solution, 600 ml of 30 per cent C.P. hydrogen

[3] J. A. LEARY, A. N. MORGAN and W. J. MARAMAN, *Plutonium Peroxide Precipitation*, Presented at the 133rd National A.C.S. Meeting at San Francisco, April 17, 1958. *Symposium on the Chemistry of the Heavy Elements.* Publication pending in *Industrial and Engineering Chemistry.*

peroxide were slowly added. The product was stirred for 30 min then filtered on a 600 ml medium fritted glass funnel and washed with 1 l. of 6 per cent hydrogen peroxide and 500 ml of absolute ethanol, after which it was air dried.

Hydrofluorination

Dry plutonium peroxide was transferred to covered platinum boats which were then sealed in a nickel tube furnace. Oxygen was passed through the furnace at 50–100 ml/min and the temperature was increased to 125°C. Hydrogen fluoride was then added at 200–300 g/hr and the temperature was increased at 50°C/15 min

TABLE 2.—CORE SAMPLES ANALYSES OF PLUTONIUM BUTTONS (p.p.m.)

Element	Button Number								
	1	2	3	4	5	7	7	8	9
Ca	<3	30	80	25	20	15	40	40	50
Al	<5	<5	<5	<5	5	<5	<5	<5	10
La	<10	<10	<10	<10	<10	<10	<10	<10	<10
Si	10	8	10	30	20	12	6	7	6
Pb	3	4	25	30	1	<1	2	1	1
Cu	15	10	25	50	8	6	<1	10	50
Ni	3	10	8	30	2	<1	1	3	10
Cr	<5	<5	<5	3	<5	<5	<5	<5	<5
Mn	15	40	25	30	30	30	25	30	25
Sn	3	1	<1	<1	<1	<1	<1	<1	4
Fe	25	25	8	10	80	80	100	80	<10
Cd	<1	<1	<1	<1	<1	5	<1	<1	<1
Zn	<20	40	50	<20	<20	<20	<20	<20	<20
C	20	27	45	55	57	20	30	17	32
Yield, wt (%)	73·1	93·0	96·9	94·5	89·4	92·8	71·1	93·0	96·11

The following analyses were the same for each button

Li	<0·2	Ba	<10
Be	<0·2	Mo	<20
Na	<5	Hg	<3
Mg	<3	Sb	<10
B	<0·5	Ag	<1
Bi	<1	As	<10
V	<20	In	<1
Co	<5	S	<5

increments to 650°C. After 4 hr at 650°C the furnace was cooled to 100°C and the plutonium tetrafluoride was removed. The procedure was varied in a few cases to include hydrofluorination at 800°C for 3 hr. The higher temperature had no apparent effect on purity of finished metal.

Reduction

A weighed portion of plutonium tetrafluoride, equivalent to 160 g of plutonium, was mixed with 77 g redistilled calcium and 51 g resublimed iodine. The charge

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was transferred to a reduction bomb which contained a high-purity calcium oxide crucible. A calcium oxide lid was placed on the crucible and the bomb lid was secured. Air was removed by evacuating and filling with argon three times after which the bomb was sealed, placed in an induction furnace and heated from room temperature to 700°C in 12 min. The exothermic reaction was indicated by a rapid increase in temperature of the outside of the bomb to 750–800°C. The same bomb was used for all reductions and was pickled with hydrochloric acid, rinsed with water and dried after each use.

The plutonium button thus produced was pickled in nitric acid, washed with water followed by absolute ethanol, dried and weighed. Samples of the top, bottom and core were taken using specially sharpened, high speed, ¼ in. drill bits.

RESULTS

Samples of all reagents and plutonium compounds were analysed chemically and spectrochemically. Table 1 contains all the data for the preparation of one of the high-purity plutonium buttons.

The tabulation of the analyses of the core drill samples of the other nine buttons in shown in Table 2.

In every case where the symbol $<$ is used, the amount was below detection limit.

Acknowledgements—The author wishes to express his gratitude to Dr. R. D. BAKER for his many helpful suggestions, to Group CMB-1 for performing the analyses, to Group CMB-8 for supplying the high-purity calcium and to Group CMB-6 for supplying the high-purity calcia crucibles necessary for this preparation.

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ORGANOMETALLIC COMPLEXES—I

THE REACTION OF METAL CARBONYLS WITH ACETYLENIC COMPOUNDS

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Abstract—A new series of organometallic complexes has been prepared by the reaction of acetylene and acetylene derivatives with carbonyls of the transition metals. A given carbonyl–acetylene system may yield as many as seven different complexes which are generally well crystallized, stable and soluble in organic solvents. It appears that these compounds are generally π-complexes in which the organic portion, usually a conjugated ring structure, is linked to the metal-carbonyl portion by the sort of interaction now familiar from aromatic and diene complexes.

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IN view of the recent developments in the chemistry of organometallic compounds it appeared to be of considerable interest to investigate in some detail the possibility of synthesizing new organometallic carbonyl complexes by the reaction of acetylene derivatives with various metal carbonyls.

The first iron–carbonyl–acetylene complexes were obtained by REPPE[1] and his co-workers by the reaction of acetylene under pressure with hydrogen derivatives of iron carbonyl. Thus when iron pentacarbonyl reacts with acetylene in aqueous ethyl alcohol the main product, apart from ethyl acrylate, is an iron-containing compound of the formula $FeC_{11}H_7O_5$, from which the two compounds $FeC_8H_4O_4$ and $FeC_7H_4O_3$ may be obtained. Furthermore, an aqueous solution of $[Fe(CO)_4H]$ Na gives, on reaction in an autoclave with acetylene under relatively mild conditions, the compound $Fe_2C_{10}H_4O_8$ in good yields. Recently several authors[2] have shown that this complex may also be prepared at room temperature and normal pressure. Similar complexes can also be obtained from alkyl-substituted acetylenes and there has been some discussion of possible structures. Thus JONES *et al.*[3] have described a "tetracarbonyliron bisphenylacetylide" of formula $FeC_{20}H_{10}O_4$ or $FeC_{20}H_{12}O_4$. Very recently STERNBERG *et al.*[4] have described the synthesis of a duroquinone–$Fe(CO)_3$ complex from $Fe(CO)_5$ and dimethylacetylene. Up to the present time the only complexes of this sort of other transition metals to be described have been the substitution products of cobalt carbonyl with several acetylene derivatives having the general formula $Co_2(CO)_6(RC_2R')$; these were described by STERNBERG *et al.*[5]

[1] W. REPPE, *Neue Entwicklungen auf dem Gebiet der Chemie des Acetylens und Kohlenoxyds* pp. 122–125. Springer-Verlag (1949).
W. REPPE and H. VETTER, *Liebigs Ann.* **582**, 136–158 (1953).
[2] I. WENDER, R. A. FRIEDEL, R. MARKBY and H. W. STERNBERG, *J. Amer. Chem. Soc.* **77**, 4946 (1955).
H. W. STERNBERG, R. A. FRIEDEL, R. MARKBY and I. WENDER, *J. Amer. Chem. Soc.* **78**, 3621 (1956).
R. CLARKSON, E. R. H. JONES, P. C. WAILES and M. C. WHITING, *J. Amer. Chem. Soc.* **78**, 6206 (1956).
[3] E. R. H. JONES, P. C. WAILES and M. C. WHITING, *J. Chem. Soc.* 4021 (1955).
[4] H. W. STERNBERG, R. MARKBY and I. WENDER, *J. Amer. Chem. Soc.* **80**, 1009 (1958).
[5] H. W. STERNBERG, H. GREENFIELD, R. A. FRIEDEL, J. WOTIZ, R. MARKBY and I. WENDER, *J. Amer. Chem Soc.* **76**, 1457 (1954).
H. GREENFIELD, H. W. STERNBERG, R. A. FRIEDEL, J. H. WOTIZ, R. MARKBY and I. WENDER, *J. Amer. Chem. Soc.* **78**, 120 (1956).

The present work constitutes a brief summary of some of the results obtained in a programme started in this laboratory in 1955, which has resulted in an extension of the chemistry of organometallic complexes. A more detailed description of the many new compounds which have been isolated as well as their preparation and their reactions will be reserved for other publications in the present series. X-ray analysis and theoretical discussion of the structures will also be reported.

I. ORGANOMETALLIC COMPOUNDS FROM IRON CARBONYLS

1. *Preparation*

For starting a systematic study of the reaction of acetylene derivatives with metal carbonyls the iron carbonyls seemed most suitable since iron forms a wide variety of different types of carbonyl compounds and all are readily obtainable.

Among these *iron dodecacarbonyl*, $Fe_3(CO)_{12}$, proved to yield the greatest variety of complexes; if $Fe_3(CO)_{12}$ is heated in inert solvents at temperatures between 60° and 100°C with various acetylenes, iron pentacarbonyl and varying quantities of carbon monoxide are obtained together with as many as seven different kinds of iron-containing complexes depending on the nature of the alkyne studied. If the acetylene derivative is liquid, the reaction can be carried out with no solvent and, as might be expected, leads to a predominance of those complexes which have larger $RC{\equiv}CR'$: Fe ratios.

If *iron enneacarbonyl*, $Fe_2(CO)_9$, is used in a similar reaction the types of the organometallic complexes obtained depend very strongly on the nature of the acetylene derivative studied. With diphenylacetylene, for example, an unstable complex is formed even at room temperature. On standing or slight heating, this decomposes into the well-crystallized compounds

$$Fe_2(CO)_6(C_6H_5C_2C_6H_5)_2 \quad \text{and} \quad Fe_2(CO)_7(C_6H_5C_2C_6H_5)_2$$

in the mole ratio 1 : 2; in the process exactly one mole of $Fe(CO)_5$ and a little carbon monoxide are produced. With other acetylene derivatives, such as phenylacetylene or the dimethyl ester of acetylenedicarboxylic acid, only dark coloured, powdery products are obtained, which in some cases no longer contain carbonyl groups.

Apart form the reaction with alkyl-substituted acetylenes described by STERNBERG *et al.*,[4] *iron pentacarbonyl*, $Fe(CO)_5$, reacts with acetylene derivatives only at high temperatures so that the experiments must be conducted in autoclaves or sealed tubes. Which of the complexes are obtained in this way is largely controlled by the reaction temperature. Thus, if $Fe(CO)_5$ and diphenylacetylene react in an inert solvent at temperatures in the range 140–160°C, the main product is $Fe(CO)_4(C_6H_5C_2C_6H_5)_2$ together with smaller quantities of $Fe_2(CO)_6(C_6H_5C_2C_6H_5)_2$. At temperatures between 200° and 240°C, on the other hand, the quantity of $Fe(CO)_4(C_6H_5C_2C_6H_5)_2$ increases and a new, very stable complex of formula $Fe(CO)_3(C_6H_5C_2C_6H_5)_2$ appears in place of the $Fe_2(CO)_6(C_6H_5C_2C_6H_5)_2$. It is especially interesting that the same two compounds can be obtained in good yields from the reaction of the acetylene in question with active iron powder and carbon monoxide under the general conditions of carbonyl synthesis.

The reactivity of polynuclear carbonyl ferrates (such as the reaction products of

iron dodecacarbonyl with methanol[6] or pyridine[7]) with acetylene derivatives was investigated, but the yield of the desired complexes is very poor.

Iron carbonyl mercury, $Fe(CO)_4Hg$ has not yielded complexes with acetylenes under any conditions so far tried. The possibly polymeric structure of the compound could be responsible for its low reactivity and its great stability. Similarly, no reaction of the iron carbonyl halides, $Fe(CO)_4I_2$ and $Fe(CO)_4Br_2$, leading to iron-containing complexes has been observed. In these cases anhydrous iron halide[8] is formed before the reaction with the acetylene can start.

Iron nitrosyl carbonyl, $Fe(CO)_2(NO)_2$, however, reacts readily with acetylene derivatives in a sealed tube. As an example, diphenylacetylene gives an easily oxidizable, deep violet complex which, in air, readily changes into a stable yellow compound. Contrary to expectation this substance does not contain NO even though in all previously known substitution reactions of iron nitrosyl carbonyl[9] only the CO is replaced by other ligands.

The reactions described above are usually carried out in an inert solvent such as petroleum ether, benzene, toluene or decalin. The choice of solvent is usually based on the reaction temperature and the solubility of reactants and products. In some cases, however, polar solvents such as methanol have proved advantageous since intermediates may be isolated as a result of their insolubility.

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2. *Types of complexes*

Nearly all the acetylene derivatives studied up to the present time form organometallic complexes with iron carbonyls. Only when both hydrogens of acetylene are substituted by very bulky groups, such as trimethyl-silyl groups, is the reaction apparently prevented by steric hindrance. In Table 1 a partial summary of the types of iron complexes so far isolated is presented, the various types being classified according to their empirical formulae. Beside the compounds listed in the table, complexes have been obtained, for example, with acetylene itself, with propargyl alcohol, and with phenylpropiolic acid and its esters. The analytical results in these cases are not yet complete but from the infra-red spectra it is almost certain that at least four further types of complex, having iron as the central atom, exist.

In general the compounds here described are stable, well-crystallized iron complexes of yellow, red or black colour. They are usually readily soluble in organic solvents. Only a few possess sharp melting points; most of them melt with decomposition, frequently above 200°C. In so far as the magnetic susceptibility has been measured the compounds were invariably found to be diamagnetic—even those in which the metal atoms may not have a rare gas configuration. All the complexes show infra-red absorption bands characteristic of terminal carbonyls; only some complexes of the empirical formula $Fe_3(CO)_8(RC_2R')_2$ show bands corresponding to bridging carbonyl groups.

In describing the preparative methods it has already been pointed out that the number and type of complexes produced are determined in considerable measure by the particular metal carbonyl used. Nevertheless the particular acetylene derivative

[6] W. HIEBER and G. BRENDEL, *Z. Anorg. Chem.* **289**, 338 (1957).
[7] W. HIEBER and R. WERNER, *Ber. Dtsch. Chem. Ges.* **90**, 286 (1957).
[8] W. HIEBER and G. BADER, *Ber. Dtsch. Chem. Ges.* **61**, 1720 (1928).
[9] W. HIEBER and J. S. ANDERSON, *Z. Anorg. Chem.* **211**, 132 (1933); W. HIEBER and D. V. PIGENOT, *Ber. Dtsch. Chem. Ges.* **89**, 613 (1956); L. MALATESTA and A. ARÀNEO, *J. Chem. Soc.* 3803 (1957).

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TABLE I.—TYPES OF COMPLEXES MADE FROM IRON CARBONYLS AND ACETYLENIC COMPOUNDS

	1 Alkyne	2 Alkynes	3 Alkynes	4 Alkynes	5 Alkynes
1 Fe		$Fe(CO)_3(RC_2R')_2$ (*a*)	$Fe(CO)_2(RC_2R')_3$ (*c*)	$Fe(CO)_3(RC_2R')_4$ (*g*)	$Fe(CO)_4(RC_2R')_5$ (*g*) (*h*)
		$Fe(CO)_4(RC_2R')_2$ (*a*) (*b*) (*e*) (*f*) (*g*) (*h*) (*i*)	$Fe(CO)_4(RC_2R')_3$ (*g*) (*h*)		
2 Fe	$Fe_2(CO)_6(RC_2R')$ (*a*) (*b*)	$Fe_2(CO)_6(RC_2R')_2$ (*a*) (*b*) (*c*) (*d*) (*e*) (*f*) (*g*) (*h*)	$Fe_2(CO_6(RC_2R')_3$ (*e*) (*g*) (*h*)		
		$Fe_2(CO)_7(RC_2R')_2$ (*a*) (*b*) (*d*) (*e*) (*f*)			
3 Fe	$Fe_3(CO)_{10}(RC_2R')$ (*e*)	$Fe_3(CO)_9(RC_2R')_2$ (*a*) (*b*) (*e*) (*f*)			

The acetylenic compounds (RC_2R') in the above table correspond to:

(*a*) = $C_6H_5C_2C_6H_5$ (*d*) = $C_2H_5C_2C_2H_5$ (*g*) = $C_6H_5C_2H$
(*b*) = $ClC_6H_4C_2C_6H_4Cl$ (*e*) = $C_6H_5C_2CH_3$ (*h*) = $BrC_6H_4C_2H$
(*c*) = $CH_3OOCC_2COOCH_3$ (*f*) = $C_6H_5C_2Si(CH_3)_3$ (*i*) = $(CH_3)_3SiC_2H$

also exerts some influence. From the above table the following generalizations are possible: apart from certain types which are formed with all substituted acetylenes there are some types which can only be formed from mono-substituted and others only with di-substituted acetylenes. Naturally, as the reaction temperature increases the more stable compounds tend to be formed at the expense of the less stable ones.

II. ORGANOMETALLIC CARBONYL DERIVATIVES OF OTHER TRANSITION METALS

With the discovery of a whole series of new types of complexes having iron as central atom it was natural to investigate whether other transition metals were also able to form corresponding organometallic compounds. With *cobalt*, apart from the compounds of formula $Co_2(CO)_6(RC_2R')$ described by STERNBERG *et al.*,[5] it has been found possible to prepare other types of complexes; for example, a tetrameric cobalt tricarbonyl substituted with diphenylacetylene can be obtained.

Among the carbonyls of group VII metals, *manganese carbonyl* gives a series of very stable complexes at reaction temperatures between 120° and 170°C.

Of the group VI hexacarbonyls, that of *tungsten* seems to produce the widest variety of organometallic complexes; one of these contains six molecules of acetylene derivative per metal atom.

The new organometallic complexes are capable of many different reactions: the CO groups can be replaced by other ligands such as phosphine or *iso*nitrile; by treatment with CO under pressure a binuclear iron complex can be transformed into a mononuclear complex, $Fe(CO)_5$ being split off in the process; some complexes react with halogens to give new halogen-containing compounds; others undergo a reaction[10] when treated with alkali.

III. STRUCTURE AND MECHANISM OF FORMATION

All available evidence indicates that the new organometallic compounds discussed here are to be regarded as π-complexes built from an organic system and one or more metal carbonyl groups, e.g. $\{Fe(CO)_3\}$. In the simplest cases, those in which only one alkyne enters the molecule, the π-electrons of the triple bond interact directly with the valence electrons of the metal.[11] However, the more common types of complexes contain more complicated organic systems—generally ring systems containing conjugated double bonds. In these cases the bonding results from interaction of the π-electrons of the double bonds with the metal in a manner similar to that in certain aromatic[12] and diene[13] complexes. Evidence for this is obtained from the study of the decomposition products. In no case so far studied has it been possible to recover the acetylene derivative itself from the compound; instead ring systems are usually found, e.g. tetraphenyl*cyclo*pentadienone from $Fe(CO)_4(C_6H_5C_2C_6H_5)_2$ or $Fe_2(CO)_7(C_6H_5C_2C_6H_5)_2$ and 1:3:5-triphenylbenzene from $Fe(CO)_4(C_6H_5C_2H)_3$ or $Fe_2(CO)_6(C_6H_5C_2H)_3$.

In the case of the complexes of composition $Fe(CO)_4(RC_2R')_2$ a new, simple

[10] W. HIEBER and F. LEUTERT, *Z. Anorg. Chem.* **204**, 145 (1932).
[11] J. CHATT, G. A. ROWE and A. A. WILLIAMS, *Proc. Chem. Soc.* 208 (1957).
[12] E. O. FISCHER and W. PFAB, *Z. Naturf.* **7 B**, 377 (1952); G. WILKINSON, M. ROSENBLUM, M. C. WHITING and R. B. WOODWARD, *J. Amer. Chem. Soc.* **74**, 2125 (1952); E. RUCH, *Sitzungsber. bayer. Akad. Wiss., Sonderdruck* Nr. 20 (1954); E. O. FISCHER, *Angew. Chem.* **67**, 475 (1955); E. O. FISCHER and W. HAFNER, *Z. Naturf.* **10 B**, 665 (1955).
[13] B. F. HALLAM and P. L. PAUSON, *J. Chem. Soc.* 642 (1958).

synthesis is possible which clearly establishes their structures as *cyclo*pentadienone-iron-tricarbonyl compounds (Fig. 1). Thus, $Fe(CO)_4(C_6H_5C_2C_6H_5)_2$ is obtained in high yields directly from tetraphenyl*cyclo*pentadienone and iron carbonyls, often under very mild conditions. Corresponding complexes can be obtained from different *cyclo*pentadienones and other metal carbonyls.

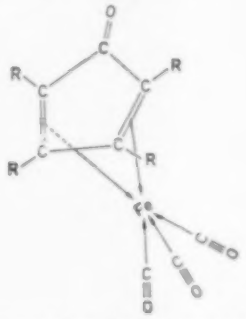

FIG. 1.—*cyclo*Pentadienone-iron-tricarbonyl.

It follows from certain theoretical considerations that compounds of the type $Fe_2(CO)_6(RC_2R')_2$ and $Fe(CO)_3(RC_2R')_2$ might be expected to contain the unknown *cyclo*butadiene ring. LONGUET-HIGGINS and ORGEL[14] have already considered the possibility that this ring might be stabilized by complex formation.

One point worthy of note is the fact that the direct reaction of acetylene derivatives with metal carbonyls leads to π-complexes which contain relatively complicated organic systems. It has been assumed as a working hypothesis that, in the reactions leading to the complexes, inherently unstable fragments of the metal carbonyls are involved. These might be produced either by the thermal decomposition of the polynuclear carbonyls or, under suitable conditions, by the reaction of the metal with carbon monoxide. This point of view is supported by the very general occurrence of $Fe(CO)_5$ among the reaction products when an alkyne is reacted with iron dodeca-carbonyl. Perhaps the primary reaction is to be formulated as:

$$Fe_3(CO)_{12} \rightarrow Fe(CO)_5 + \{Fe(CO)_4\} + \{Fe(CO)_3\}$$

If more stable carbonyls are used as starting materials in this reaction, e.g. $Fe(CO)_5$ itself, the reaction temperature must be increased accordingly.

The carbonyl fragments produced in the above way may either lose carbon monoxide to form simpler residues or, especially in the case of $\{Fe(CO)_3\}$, they may initially add an alkyne molecule. Further stereospecific additions of alkynes or carbon monoxide can then lead, through ring closure, to stable complexes. This proposed mechanism explains most of the observed reactions except those which proceed well below the decomposition temperature of the metal carbonyl. In such cases substitution reactions must play a dominant role. They may be expected to be especially important when the basic structure of the carbonyl is not greatly altered in forming the complex, for example, in the formation of $Co_2(CO)_6(RC_2R')$[5] from $Co_2(CO)_8$ or of $Co_4(CO)_{10}(RC_2R')$ from $Co_4(CO)_{12}$.

It is evident from several of the above examples that reactions in which the new

[14] H. C. LONGUET-HIGGINS and L. E. ORGEL, *J. Chem. Soc.* 1969 (1956).

complexes here described play leading roles may be expected to provide attractive synthetic methods for preparing certain classes of organic compounds. That this is indeed so and that the family of π-complexes is much larger than originally supposed will be shown in further detail in forthcoming publications.

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INFRA-RED SPECTRA OF 1:10-PHENANTHROLINE METAL COMPLEXES IN THE ROCK SALT REGION BELOW 2000 cm^{-1}

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Abstract—Infra-red spectra of twenty two metal–1:10-phenanthroline perchlorates together with spectra of the free ligand, its hydrate and perchlorate salt have been obtained in the region between 600 and 2000 cm^{-1} from Nujol mulls. In general, the spectra of the complexes were remarkably similar in their gross features and no obvious correlations with magnetic or other physical properties were noted. However, the results provide evidence for co-ordination in the case of the alkali metal complexes and also indicate a co-ordination number of eight in the alkaline earth, lead and manganese complexes. The compositions of all compounds studied were confirmed by elementary microanalysis and the list includes several new compounds as well as a few having compositions differing slightly from those previously reported. The interpretation of the principal features of the spectra is discussed.

ALTHOUGH an increasing number of papers reporting on the infra-red spectra of metal co-ordination complexes have appeared in the recent literature, the results available are not yet adequate for a proper assessment of this technique's value, apart from its usefulness in characterization and identification. Most of the studies which have appeared to date have dealt with complexes involving either very simple ligands such as NH_3 or CN^-,[1–4] or with ligands having a co-ordinating group which can be associated with a characteristic vibration frequency such as β-diketones[5] or compounds containing —COOH or —NH_2 groups.[6–8] Very few data have been presented for compounds where the complexing agent is a fairly large and complicated molecule. In general, more or less marked alterations in the spectrum of the ligand have been reported to occur upon co-ordination, and in some cases it has been possible to interpret these changes satisfactorily in terms of the structure or geometry of the complex, or to relate them to changes in bonding in the ligand. It has also been found that these changes in the ligand spectrum are relatively insensitive to the nature of the metal involved such that disappointingly little has been learned about the metal to ligand bond.

In the present work, the infra-red spectra of a number of heavy metal complexes with 1:10-phenanthroline have been obtained together with the spectra of several alkali and alkaline earth complexes, acid salts and the hydrate. For comparison purposes, the spectra of a small number of 2:2-bipyridine complexes were also

[1] D. B. POWELL and N. SHEPPARD, *J. Chem. Soc.* 3108 (1956).
[2] G. M. BARROW, R. H. KRUEGER and F. BASOLO, *J. Inorg. Nucl. Chem.* **2**, 340 (1956).
[3] L. H. JONES, *J. Chem. Phys.* **26**, 1578 (1956); **27**, 468, 665 (1957).
[4] G. F. SVATOS, D. M. SWEENY, S. MIZUSHIMA, C. CURRAN and J. V. QUAGLIANO, *J. Amer. Chem. Soc.* **79**, 3313 (1957).
[5] H. F. HOLTZCLAW and J. P. COLLMAN, *J. Amer. Chem. Soc.* **79**, 3318 (1957).
[6] M. L. MORRIS and D. H. BUSCH, *J. Amer. Chem. Soc.* **78**, 5178 (1956).
[7] R. B. PENLAND, S. MIZUSHIMA, C. CURRAN and J. V. QUAGLIANO, *J. Amer. Chem. Soc.* **79**, 1575 (1957).
[8] K. NAKAMOTO, J. FUJITA, S. TANAKA and M. KOBAYASHI, *J. Amer. Chem. Soc.* **79**, 4904 (1957).

obtained. The anion present in all cases was perchlorate which was selected because it gave nicely crystalline salts which could be easily handled. Since many complexes of 1:10-phenanthroline have not been completely characterized, or doubtful points are present in the literature preparations, all compounds were subjected to elemental microanalysis before their spectra were accepted. In several cases, the compositions determined by the analytical data represented new compounds or minor variations from the compounds previously reported.

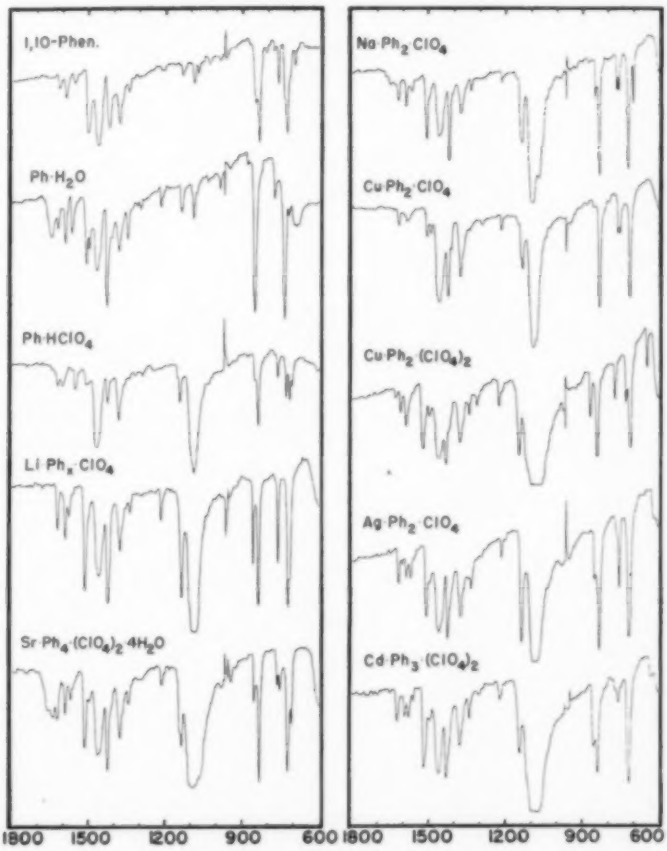

FIG. 1.—Infra-red spectra of 1:10-phenanthroline and its hydrate, perchlorate and some of its metal complexes as Nujol mulls.

The spectral results are of interest in connexion with questions regarding the metal co-ordination number in certain complexes and also provide a limited amount of information regarding bonding in the complexes.

EXPERIMENTAL RESULTS

Spectra of the 1:10-phenanthroline metal complexes, the spectrum of the free base, its hydrate and perchlorate salt are shown in Figs. 1–3 while the measured frequencies of the band maxima are given in Table 1. Similar information for the bipyridine complexes is given in Table 2 and selected spectra are shown in Fig. 3.

Inspection of the results shows that in their gross features, the spectra of the various phenanthroline complexes are remarkably similar in appearance and show no obvious correlations either with magnetic or other physical properties of the complexes, with the valence of the metal or with the number of ligand groups co-ordinated. Since the vibrational frequencies observed in the rock salt region arise exclusively in the ligand part of the complex, which, in this case, is fairly large and complex, it is perhaps not surprising that the spectra do not vary markedly from metal to metal.

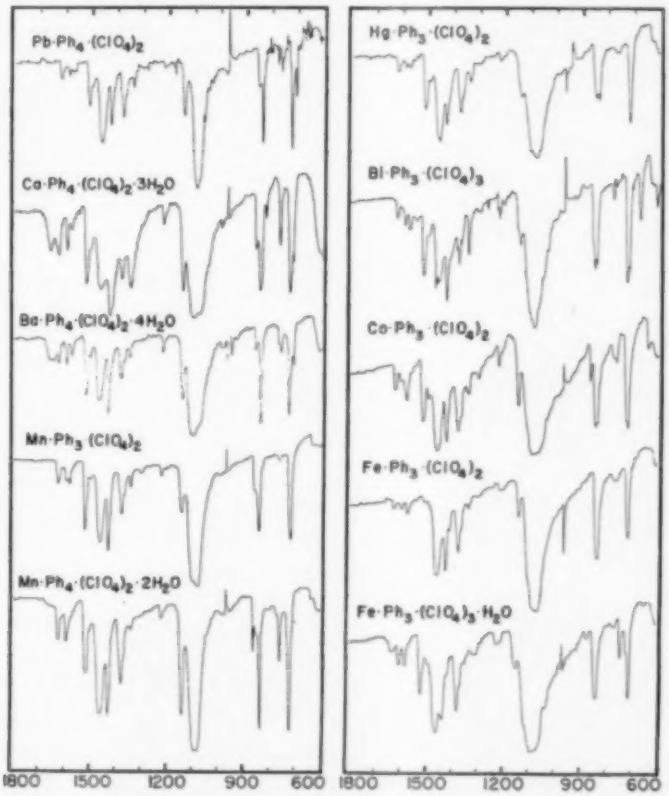

FIG. 2.—Infra-red spectra of some metal complexes of 1:10-phenanthroline from Nujol mulls.

Similar observations have been made elsewhere in studies involving simpler ligands.

More detailed examination of the spectra shows that the metal complexes are easily distinguishable from either the free base, the hydrate or the acid salt and this provides a satisfactory method of detecting the presence of occluded or uncomplexed ligand. For example, phenanthroline perchlorate can be identified in mixtures by a strong band at 1544 cm^{-1} since the corresponding band in the metal complexes is confined to the range between 1510 and 1530 cm^{-1}. Several other acid salts were also examined in the course of this investigation including the chloride, bromide, nitrate and sulphate. In all cases the band mentioned fell consistently outside the range of the same band in the metal complexes. Differentiation of the free base or the hydrate from the metal complexes requires more careful comparison since no single band

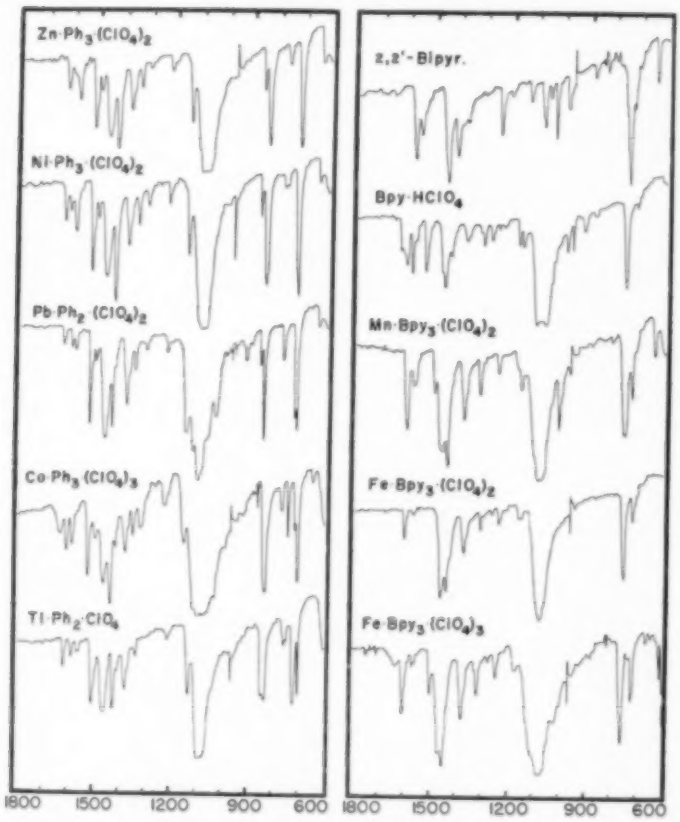

FIG. 3.—Infra-red spectra of some metal complexes of 1:10-phenanthroline and 2:2′-bipyridine from Nujol mulls.

can be selected which will give an unequivocal answer as in the case of the acid salts. Detailed comparison of the bands in the 700–900 cm^{-1} region appears most suitable.

The spectra of the metal complexes themselves differed in minor respects such that no two were identical, although the cobalt and nickel were nearly so. Principal differences occurred in the 700–900 cm^{-1} region and consisted of varied patterns in the splitting of the strong bands near 720 and 850 cm^{-1}.

The results for the Li, Na and alkaline earth complexes are of some interest in view of questions raised[9] as to whether the alkali metals actually are chelated in the complexes, and in regard to the high co-ordination number observed for the alkaline earths. Since experimental limitations prevented study of the spectral region in which frequencies associated with the metal–nitrogen bond might be expected, the evidence bearing on these two questions is somewhat indirect. However, in the case of the heavy transition metal complexes, certain modifications of the spectrum of the free ligand occurred which appear to be characteristic of the ligand in the bound state. Perhaps the most obvious of the alterations was a general shift of the ring vibrations in the 1400–1600 cm^{-1} region to higher frequency. These modifications were clearly present

[9] W. W. BRANDT, F. P. DWYER and E. C. GYARFAS, *Chem. Rev.* **54**, 959 (1954).

TABLE 1.—INFRA-RED FREQUENCIES OF METAL 1:10-PHENANTHROLINE PERCHLORATES IN THE NaCl REGION BELOW 2000 cm^{-1}

P‡	PH_2O	$PHClO_4$	LiP†	NaP_2	CaP_3†	SrP_3	BaP_3	$Mn^{II}P_3$	$Mn^{III}P_3$	$Fe^{II}P_3$	$Fe^{III}P_3$	$Co^{II}P_3$	$Co^{III}P_3$	$Ni^{II}P_3$	$Cu^{I}P_2$	$Cu^{II}P_2$	$Ag^{I}P_2$	ZnP_3	CdP_3	$Hg^{II}P_3$	$Tl^{I}P_2$	$Pb^{II}P_4$	$Pb^{II}P_2$	$Bi^{III}P_3$
		612	610	613							610		613			610								614
704	695	711	713	711	718	714	712	660	611		655	612	656	610		652					612	608		633
722	707		722	725		724			640	719		643	714	647	607		610	612	611		613	667	667	676
	723								667								720	645	640	611	710	712		718
734*	738*	717*	731*	730*	730*	729*	729*	726*	724*	724*	713*	724*	717*	723*	721*	718*	726*	726*	722*	723*	730*	729*	720*	728*
		782									722												728	
		816	766	766	770	760	760	762	727			729	726	728		735			727*	729			760	771
744	779		777	774		771	770		731		747		753	766	760				732					
767				810	824				762	765		767	778	779	768	777	764	769	767	767	760	767	773	781
783			845	830					775	777	775	780	796				770	773	778	777	768			786
813									781	838	839	843	844	842					788	789	775	808		846
842*	854*	847*	850*	843*	845*	839*	838*	838*	848*	846*	844*	849*	847*	848*	838*	847*	840*	848*	843*	843*	839*	842*	847*	854*
		855																						862
		884							858						840		850		853	853		849		930
		889							867	849	878	869	884		863	874	860	868	858	860	855	859	862	942
	884	931											930	869	954	930	961	930	868	864		890	896	1008
	989	981	860	858	862	861	859	856			1035		1039			977	987		933	934		958	1030	1036
854	1033	994	874	992	992		950	865											1002	1000		988		1053
	1080		887			950	990	991														1036		
876																						1047		
993																								
1029																								
1075																								
1092	1093	1088*	1087*	1088*	1090*	1103*	1100*	1093*	1090*	1085*	1085*	1086*	1085*	1085*	1095*	1090*	1090*	1090*	1080*	1083*	1080*	1090*	1090*	1100*
		1145													1140			1148					1145	
	1139	1158							1148	1147	1152	1149	1157	1148	1146	1150			1147	1148	1137		1210	1143
	1142	1192	1140	1145*	1144	1143	1141	1144*	1217	1208	1213		1212				1143*			1157				1151
	1219	1228		1220	1221	1150			1226	1223	1225	1224		1224	1222	1227	1222	1227		1220	1220	1144*	1302	1207
1137		1244	1223			1217	1218	1222					1231		1298				1228	1229		1208	1345	1223
1217	1297	1287	1257						1306		1315	1305		1305		1315	1339	1309	1308	1310		1222	1423	1306
		1320	1289						1345	1342		1342	1327	1341		1345	1350	1344	1344	1344	1342	1300		1346
1346	1349	1340	1342	1339	1347	1347	1348	1339			1350	1347	1353									1342		1416
		1370								1416	1419		1420		1418	1425					1415	1422		
				1413*																		1429		
	1410	1419	1420	1420																			1435	
1423*	1427*	1428	1426*	1426	1430*	1431*	1430*	1432*	1431*	1431*	1432*	1430*	1439*	1429*	1428*	1436*	1433*	1434*	1433*	1436*		1429*	1500	
	1497	1473*	1499	1503	1500	1498	1498	1500	1499	1493	1497	1499	1499	1499	1496	1499	1500	1500	1501	1502	1507	1500	1512	1431*
		1502																						1500
1505*	1508*	1544*	1513*	1512*	1518*	1518*	1516*	1519*	1520*	1515	1523	1522*	1527*	1521*	1510	1525*	1515*	1522*	1519	1518*	1515	1513*	1520	1521
1558	1565		1571	1572	1575	1572	1570		1581	1580	1585	1583	1589	1584	1576	1590							1542	
1591	1590	1599	1591	1592	1594	1593	1592	1592	1592	1602	1607	1605	1610	1606	1588	1610							1560	1550
1615	1618	1618	1623	1622	1624	1624	1620	1607	1624	1632	1633	1627	1638	1626	1620	1629	1575	1585	1580	1578	1570	1574	1575	1575
	1645	1635			1658	1642	1640	1622									1593	1607	1593	1592	1593	1591	1591	1593
																	1622	1627	1624	1624	1624	1623	1622	1624

* Indicates the more intense bands.
† See Experimental section for analytical results.
‡ P = 1:10-phenanthroline. See Experimental section for complete formulae of salts.

TABLE 2.—INFRA-RED FREQUENCIES OF SOME METAL 2:2′-BIPYRIDINE PERCHLORATES IN THE NaCl REGION BELOW 2000 cm^{-1}

B†	$BHClO_4$	$Mn^{II}B_3$	$Fe^{II}B_3$	$Fe^{III}B_3$	$Co^{II}B_3$	$Co^{III}B_3$	$Ni^{II}B_3$
652		650		669	652		650
	722	720	720	722		720	717
739		736	728	726	735	724	732
				741			
755*	763*	762*	763*	764*	766*	763*	763*
		767	768	797	774	792	771
892	888	810		889	889	889	886
	926		954	932			927
992	994	973	997		964		961
	1020			1020	1021		1005
1041	1042	1007		1030	1045	1036	1016
1065	1050						1021
		1018	1070		1072		
		1045					
1085	1070*	1088*	1084*	1080*	1085*	1088*	1083*
1090							
	1112						
1140	1161	1161	1160	1170	1158	1166	1156
	1177	1175	1167	1180	1172	1177	1169
	1234				1218		1217
1252	1253	1247	1242	1247	1248	1246	1246
	1281		1272	1278			
	1312		1315		1317		1313
	1324	1320		1321		1320	
				1370			
1421*	1370	1446*	1448*	1456*	1446*	1455*	1445*
					1474		
		1496		1503	1498		1496
	1537*					1505	
1560	1576	1570	1569	1567	1566	1570	1564
1583*	1589	1576			1576		1574
	1610	1601*	1607	1608	1604*	1609	1603*
	1622			1630			
	1633	1608					

* Indicates the more intense bands.
† B = 2:2′-bipyridine. See Experimental section for complete formulae of salts.

in both the lithium and sodium complexes as well as those of the alkaline earths, although the magnitude of the shifts was not as great as for the heavy metals. Since no bands attributable to the free base or its hydrate were observed, one is led to conclude that all the phenanthroline present in these light metal complexes is co-ordinated. This conclusion is supported by the observation that no ligand was lost when the compounds were heated *in vacuo* at 110°C. The analytical data confirm the presence of four (bidentate) ligands in the strontium and barium complexes and between three and four for calcium. Similarly, the spectral and analytical data support a co-ordination number of eight for manganese(II) and lead(II) in their tetrakis complexes.

However, the spectra of literature preparations with tin(II) give no evidence of co-ordination and showed only the lines of phenanthroline perchlorate.

Co-ordination involving protons, either in water or from an acid, produced the same characteristic shifts as co-ordination to a metal. In the case of water, the magnitude of the effects was small, smaller even than for the alkali and alkaline earth metals, but in the salts of strong acids where the proton is bound firmly to the nitrogen atom, the shifts were quite striking.

DISCUSSION OF THE SPECTRAL RESULTS

No general, systematic study of the vibrational frequencies of heterocyclic aromatic compounds has appeared in the literature and even the spectra of polycyclic aromatic hydrocarbons have not been dealt with at all extensively. BELLAMY,[10] and JONES and SANDORFY[11] however, indicate that many of the generalizations based on studies of benzene derivatives may be carried over quite successfully to polycyclic molecules and that the introduction of a heteroatom into a ring usually results in only minor changes in the characteristic skeletal frequencies of the corresponding hydrocarbon. In its effect on the frequencies associated with the hydrogen atoms attached to the ring, the heteroatom behaves as a substituted carbon atom.

In the spectra of the phenanthroline complexes between 600 and 2000 cm^{-1}, strong bands were observed in three frequency regions, namely between 700 and 900 cm^{-1}, between 1125 and 1250 cm^{-1}, and between 1400 and 1650 cm^{-1}. Nujol bands prevented observation of bands in the neighbourhood of 1380 and 1465 cm^{-1} while a very intense band due to the perchlorate anion obliterated frequencies due to the ligand in a region about 70 cm^{-1} wide centered around 1085 cm^{-1}. Strong bands in the 700–900 cm^{-1} region in spectra of aromatic hydrocarbons have been identified with motions of ring hydrogen atoms moving in phase out of the plane of the ring. The particular frequency at which such bands appear further has been shown to depend on the number of adjacent hydrogen atoms around the ring and has been used to determine substitution patterns. In phenanthroline, and also its complexes, two strong bands appeared at approximately 725 and 850 cm^{-1}. This is the number expected since there is one group of two and two groups of three adjacent hydrogen atoms in the ring system. In hydrocarbons, the frequency shifts upwards as the number of adjacent atoms in a group decreases. On this basis, the 725 cm^{-1} band is assigned to the out of plane motion of the hydrogen atoms on the heterocyclic rings and the 850 cm^{-1} band to the hydrogens on the centre ring. The multiple splittings which these bands exhibited in most of the spectra probably arise from out-of-plane hydrogen motions other than the one in which all atoms move in phase, and also possibly from overtones of low lying fundamentals in resonance. In the bipyridyl spectra, only one strong band was observed in this region as expected for two identical groups of four hydrogen atoms each. The pattern of splitting of all these bands appeared quite sensitive to small differences in the nature of the co-ordinated atom since this region of the spectrum was most characteristic of any given complex. The variations did not appear systematic however.

Not much can be said about the bands in the 1125–1250 cm^{-1} region except that

[10] L. J. BELLAMY, *The Infra-red Spectra of Complex Molecules*. John Wiley, New York (1954).
[11] R. N. JONES and C. SANDORFY, *Chemical Applications of Spectroscopy*, Vol. IX, *Technique of Organic Chemistry* Chap. V. Interscience Publishers, New York (1956).

they may arise from in-plane hydrogen deformation motions or possibly ring vibrations. Even in the case of many simple aromatic compounds, satisfactory assignments for bands in this part of the spectrum are not available. The observed positions of the bands in the complexes varied somewhat from metal to metal but the shifts were scarcely large enough to justify any attempts at correlations.

It is in the third region that characteristic ring frequencies of aromatic compounds occur, both in monocyclic and polycyclic compounds and in heterocyclic as well as

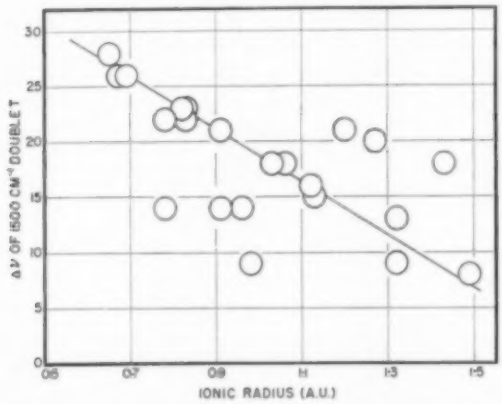

FIG. 4.—Separation between the two components of the 1500 cm^{-1} doublet vs. the ionic radius of the metal ion in 1:10-phenanthroline complexes.

carbocyclic. Perhaps the most typical and usually the most intense of these ring frequencies are one close to 1500 cm^{-1} and a second in the neighbourhood of 1600 cm^{-1}, the latter often consisting of more than one maximum. For example, in phenanthrene the first occurs[12] at approximately 1500 cm^{-1} and the second at about 1605 cm^{-1} with a second component some 25 cm^{-1} or so higher. A third strong band occurs at about 1450 cm^{-1}. The spectrum of 1:10-phenanthroline is quite similar, the one band occurring at 1505 cm^{-1}, the second appearing as a triplet with the centre component at 1590 cm^{-1} and the third band shifting to 1423 cm^{-1}. Reference has been made previously to the fact that all these bands move to higher frequencies on coordination. The 1423 cm^{-1} band was least sensitive in this respect but the other two showed a clearly discernable shift of the order of 10 to 25 cm^{-1}. In addition, in all the complex spectra observed, the 1505 cm^{-1} band exhibited a weak satellite on its low frequency side. In some of the spectra, this component was present as a shoulder but in most it appeared as a sharp and well defined, though weak, band. The separation of the two maxima varied from metal to metal and several correlations with various properties of the metal ion were tried. It was found that the splitting varied in a direct manner with the ionic radius of the metal ion although the relationship was not as striking as one might wish since the magnitude of the separation did not exceed 30 cm^{-1} in any one case. The correlation is shown in Fig. 4. Similar, though not quite as good, correlations with the ionic radius were also noted for the mean position of the triplet at 1600 cm^{-1}, and for the separation between the 725 and 850 cm^{-1} bands.

[12] C. G. CANNON and G. B. B. M. SUTHERLAND, *Spectrochim. Acta* **4**, 373 (1951).

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These observations suggest that the size and consequent polarizing effect of the metal ion exercises a small but observable influence on the distribution of the electrons in the ring system. Co-ordination of the phenanthroline to a proton instead of to a metal ion resulted in a significantly greater splitting of the 1500 cm^{-1} band and also greater shifts of the other bands. Since the proton has a much small size and consequently a greater polarizing effect, the electrostatic picture is consistent.

The spectra of 2:2′-bipyridine and its complexes in general were less complicated than those of phenanthroline. Only three strong bands were present, one near 760 cm^{-1} ascribed to out of plane bending of ring hydrogens as mentioned previously, one near 1450 cm^{-1} which is probably a ring frequency, and a ring frequency near 1600 cm^{-1}. Numerous weak bands were observed between 900 and 1300 cm^{-1}. No close similarity to the phenanthroline spectra was noted except for the two ring frequencies. The absence of a strong band near 1500 cm^{-1} suggests that this particular ring frequency in the phenanthroline compounds is associated with the carbocyclic ring. No correlations with properties of the metal were apparent although the small number of complexes examined made attempts difficult.

EXPERIMENTAL

Spectroscopic. The infra-red absorption spectra were obtained with a Perkin–Elmer Model 21 spectrometer equipped with NaCl optics. All substances were examined as Nujol mulls. The frequencies tabulated for the various bands are considered to have an uncertainty of ± 5 cm^{-1} below 1800 cm^{-1} while the reproducibility generally was ± 1 cm^{-1} on the sharp bands and ± 2 cm^{-1} on most of the rest. Due to the presence of Nujol bands, the hydrogen stretching region yielded little information except to confirm the existence of a hydrate where it existed.

Analytical. All compounds were analysed for nitrogen and, wherever practicable, for metal content and carbon and hydrogen.* Since most of the compounds undergo violent decomposition on heating, melting points were not determined. The 1:10-phenanthroline monohydrate and 2:2′-bipyridine were obtained from the G. Frederick Smith Chemical Co. and used without further purification.

1:10-*Phenanthroline.* The anhydrous material was obtained on drying the monohydrate *in vacuo* at 110°C over phosphorous pentoxide.

1:10-*Phenanthrolium perchlorate.* The salt was isolated as an amorphous precipitate after adding a slight excess of perchloric acid to an aqueous solution of the free base. Recrystallization from water converted the product into glistening white needles. (Found: C, 51·2; H, 3·15; N, 9·94. Calc. for Phen. $HClO_4$: C, 51·4; H, 3·21; N, 9·97%).

Lithium complex. Attempts to isolate a lithium complex of definite composition following the procedure reported by PFEIFFER and CHRISTELEIT[13] for the preparation of mono-(1,10-phenanthroline)-lithium(I) perchlorate were unsuccessful. The products obtained most likely were mixtures of complexes since the spectra showed no significant absorption due to free ligand, its hydrate or its perchlorate salt. The following analysis was obtained for the material whose spectrum is presented. (Found: Li, 1·34; C, 60·7; H, 4·12; N, 10·4. Calc. for $LiC_{12}H_8N_2ClO_4$: Li, 2·41; C, 50·4; H, 2·79; N, 9·77. Calc. for $Li(C_{12}H_8N_2)_2ClO_4$: Li, 1·48; C, 61·7; H, 3·42; N, 12·0%).

Bis-(1:10-*phenanthroline*)-*sodium*(I) *perchlorate.* Prepared according to the method of PFEIFFER and CHRISTELEIT[13] who report the air dried substance to be the trihydrate. In the present work, the air dried product suffered no loss in weight on drying *in vacuo* over P_2O_5 at 110°. Found: C, 59·4; H, 3·24; N, 11·7. Calc. for $Na(C_{12}H_8N_2)_2ClO_4$: C, 59·7; H, 3·31, N, 11·6%).

Tetra-(1:10-*phenanthroline*)-*calcium*(II) *perchlorate trihydrate.* A pure product could not be isolated according to the method in the literature.[13] Since the infra-red spectrum closely resembled those of the other alkaline earth metals and showed no bands attributable to uncomplexed ligand, it has

* Carbon, hydrogen and nitrogen analyses were carried out by Spang Microanalytical Laboratories, Ann Arbor, Michigan.

[13] P. PFEIFFER and W. CHRISTELEIT, *Z. Anorg. Chem.* **239,** 133 (1938).

been included. The analysis suggests that the material is a mixture of the tris- and tetra-(1:10 phenanthroline) calcium(II) perchlorates. (Found: C, 52·4; H, 3·51; N, 11·9; Ca, 4·58; H_2O, 5·50. Calc. for $Ca(C_{12}H_8N_2)_4(ClO_4)_2 \cdot 3H_2O$: C, 56·7; H, 3·74; N, 11·0; Ca, 3·95; H_2O, 5·32%).

Tetra-(1:10-*phenanthroline*)-*strontium*(II) *perchlorate tetrahydrate*. The method of PFEIFFER and CHRISTELEIT[13] was followed. (Found: C, 53·2; H, 3·81; N, 10·2; Sr, 8·18; H_2O, 6·94. Calc. for $Sr(C_{12}H_8N_2)_4(ClO_4)_2 \cdot 4H_2O$: C, 53·5; H, 3·71; N, 10·4; Sr, 8·11; H_2O, 6·67%).

Tetra-(1:10-*phenanthroline*)-*barium*(II) *perchlorate tetrahydrate*. The literature procedure[13] was followed. (Found: C, 50·8; H, 3·44; N, 10·0; Ba, 12·11; H_2O, 6·33. Calc. for $Ba(C_{12}H_8N_2)_4(ClO_4)_2 \cdot 4H_2O$: C, 51·1; H, 3·54; N, 9·92; Ba, 12·17; H_2O, 6·38%).

Tetra-(1:10-*phenanthroline*)-*manganese*(II) *perchlorate dihydrate*. A solution of 0·17 g of $MnSO_4 \cdot H_2O$ and 0·60 g of the phenanthroline monohydrate in 100 ml of hot water was treated with 0·25 g of sodium perchlorate. Colourless needles were obtained after recrystallization of the precipitate from water. (Found: C, 57·9; H, 3·68; N, 11·1; Mn, 5·36; H_2O, 4·3. Calc. for $Mn(C_{12}H_8N_2)_4(ClO_4)_2 \cdot 2H_2O$: C, 57·1; H, 3·56; N, 11·1; Mn, 5·43; H_2O, 3·6%).

Tris-(1:10-*phenanthroline*)-*manganese*(II) *perchlorate*. This compound was obtained as a pale yellow powder upon heating the tetra complex *in vacuo* at 185° over P_2O_5. (Found: C, 54·3; H, 3·24; H, 10·6; Mn, 6·81. Calc. for $Mn(C_{12}H_8N_2)_3(ClO_4)_2$: C, 54·4; H, 3·04; N, 10·6; Mn, 6·91%).

Tris-(1:10-*phenanthroline*)-*iron*(II) *perchlorate*. Prepared by adding 0·30 g of sodium perchlorate to a solution of 0·39 g $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ and 0·60 g of the phenanthroline monohydrate in 50 ml of hot water. Recrystallization of the amorphous product from hot water gave dark red crystals. (Found: C, 54·2; H, 3·10; N, 10·2. Calc. for $Fe(C_{12}H_8N_2)_3(ClO_4)_2$: C, 54·4; H, 3·02; N, 10·6%).

Tris-(1:10-*phenanthroline*)-*iron*(III) *perchlorate monohydrate*. Chlorine gas was introduced into a solution of 0·30 g of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$, 0·60 g of phenanthroline monohydrate and 0·2 ml of concentrated H_2SO_4 in 100 ml of water until the colour changed from red to light blue. A moderate excess of 30% $NaClO_4$ solution was then added and the mixture cooled in an ice bath. The blue crystalline product was washed several times with small portions of cold water and dried *in vacuo* at room temperature over Dehydrite. If not protected from sunlight, the isolated product slowly turned red in colour. (Found: C, 45·8; H, 2·86; N, 9·18; H_2O, 2·10. Calc. for $Fe(C_{12}H_8N_2)_3(ClO_4)_3 \cdot H_2O$: C, 47·4; H, 2·85; N, 9·20; H_2O, 1·97%).

Tris-(1:10-*phenanthroline*)-*cobalt*(II) *perchlorate*. A solution of 0·24 g of $CoCl_2 \cdot 6H_2O$ in 20 ml of ethanol was heated to boiling, treated successively with 0·60 g of phenanthroline monohydrate, 0·30 g of $NaClO_4$ and 200 ml of boiling water and then stored immediately in an evacuated desiccator. After 24 hr, the yellow-brown crystalline product was isolated, washed with small portions of water, and dried *in vacuo* at room temperature. (Found: C, 53·1; H, 3·15; N, 10·5. Calc. for $Co(C_{12}H_8N_2)_3(ClO_4)_2$: C, 54·2; H, 3·04; N, 10·5%).

Tris-(1:10-*phenanthroline*)-*cobalt*(III) *perchlorate dihydrate*. A solution of 0·24 g of $CoCl_2 \cdot 6H_2O$, 0·60 g phenanthroline monohydrate, 2 ml hydrogen peroxide (30 per cent) and 2 ml concentrated HCl in 50 ml distilled water was evaporated to approximately 5 ml. On treating the resulting syrupy mixture with 100 ml of water followed by 1 ml perchloric acid (72 per cent), a golden yellow precipitate formed. Recrystallized from 50 ml of water containing 1 ml 30% hydrogen peroxide. (Found: C, 46·5; H, 3·06; N, 9·03; H_2O, 4·06. Calc. for $Co(C_{12}H_8N_2)_3(ClO_4)_3 \cdot 2H_2O$: C, 46·4; H, 3·00; N, 9·00; H_2O, 3·86%).

Tris-(1:10-*phenanthroline*)-*nickel*(II) *perchlorate hemihydrate*. Nickelous perchlorate was prepared *in situ* by treating 0·24 g of $NiCO_3$ with excess perchloric acid followed by evaporation to near dryness. After dissolving in 50 ml of water, the solution was treated with 1·2 g of phenanthroline monohydrate, heated for several minutes near boiling and then allowed to cool to room temperature. The resulting rose-red precipitate was recrystallized from water. (Found: C, 53·3; H, 3·18; N, 9·93; H_2O, 1·08. Calc. for $Ni(C_{12}H_8N_2)_3(ClO_4)_2 \cdot \frac{1}{2}H_2O$: C, 53·6; H, 3·10; N, 10·4; H_2O, 1·11%).

Bis-(1:10-*phenanthroline*)-*copper*(I) *perchlorate*. Prepared by adding a solution of 0·40 g phenanthroline monohydrate in 25 ml ethanol to a boiling solution containing 0·25 g $CuSO_4 \cdot 5H_2O$, 0·2 g hydroxylamine hydrochloride, 1 ml conc. aqueous ammonia and 100 ml of water. While still boiling, the solution was treated with a slight excess of 10% $NaClO_4$ solution and the dark violet precipitate produced was further digested for 1 hr on the steam bath. The final product was washed well with water and dried at room temperature *in vacuo* over magnesium perchlorate. (Found: C, 55·3; H, 3·27; N, 10·7; Cu, 12·22. Calc. for $Cu(C_{12}H_8N_2)_2ClO_4$: C, 55·2; H, 3·08; N, 10·7; Cu, 12·14%).

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Bis-(1:10-*phenanthroline*)-*copper*(II) *perchlorate*. Cupric perchlorate was prepared *in situ* by dissolving 0·08 g CuO in excess perchloric acid, evaporation to near dryness and dissolution in 100 ml distilled water. After heating to near boiling, 0·50 g phenanthroline monohydrate were added to this solution and the resulting amorphous blue-green precipitate was digested several hours on a steam bath. The crystalline product obtained was recrystallized from 80 ml of boiling methanol and dried *in vacuo* at room temperature. (Found: C, 46·2; H, 3·15; N, 9·11; Cu, 10·16. Calc. for $Cu(C_{12}H_8N_2)_2(ClO_4)_2$: C, 46·2; H, 2·56; N, 9·00; Cu, 10·19%).

Bis-(1:10-*phenanthroline*)-*silver*(I) *perchlorate*. Prepared by adding 0·13 g $NaClO_4$ to a solution of 0·17 g $AgNO_3$ and 0·60 g phenanthroline monohydrate dissolved in a mixture of 200 ml water and 200 ml methanol. The amorphous precipitate was digested 1 hr on a steam bath, filtered and recrystallized twice from nitrobenzene. The pale yellow crystalline product was dried *in vacuo* at room temperature. (Found: C, 51·2; H, 2·87; N, 9·93; Ag, 19·2. Calc. for $Ag(C_{12}H_8N_2)_2ClO_4$: C, 50·8; H, 2·82; N, 9·86; Ag, 19·0%).

Tris-(1:10-*phenanthroline*)-*zinc*(II) *perchlorate*. A zinc perchlorate solution was prepared by dissolving 0·10 g zinc chloride in excess perchloric acid, evaporating nearly to dryness and redissolving in 200 ml distilled water. This solution was heated nearly to boiling, 0·60 g phenanthroline monohydrate were added and the mixture allowed to cool and stand overnight. The crystalline product obtained was washed with small portions of cold water, dissolved in a small amount of hot water and allowed to crystallize slowly. The final product was in the form of glistening needles with a slight tinge of pink suggesting a trace of iron contamination. (Found: C, 53·8; H, 3·08; N, 10·6. Calc. for $Zn(C_{12}H_8N_2)_3(ClO_4)_2$: C, 53·7; H, 2·98; N, 10·4%).

Tris-(1:10-*phenanthroline*-*cadmium*(II) *perchlorate*. A cadmium perchlorate solution was prepared by dissolving 0·12 g of the metal in a mixture of 1 ml conc. HNO_3 and 1 ml 72% $HClO_4$, evaporating to dryness, and redissolving in 200 ml water. The complex was prepared in the same manner as the zinc complex. (Found: C, 50·7; H, 3·11; N, 9·70. Calc. for $Cd(C_{12}H_8N_2)_3(ClO_4)_2$: C, 50·7; H, 2·82; N, 9·85%).

Tris-(1:10-*phenanthroline*)-*mercury*(II) *perchlorate*. This substance was obtained in the form of glistening white needles by following the procedure described for the zinc complex. (Found: Hg, 21·1; N, 8·76. Calc. for $Hg(C_{12}H_8N_2)_3(ClO_4)_2$: Hg, 21·3; N, 8·94%).

Bis-(1:10-*phenanthroline*)-*thallium*(I) *perchlorate*. Prepared according to the procedure of PFEIFFER and WERDELMANN.[14] (Found: C, 43·5; H, 2·41; N, 8·77; Tl, 30·0. Calc. for $Tl(C_{12}H_8N_2)_2ClO_4$: C, 43·4; H, 2·41; N, 8·44; Tl, 30·6%).

Tetra-(1:10-*phenanthroline*)-*lead*(II) *perchlorate*. Prepared by the method of PFEIFFER and CHRISTELEIT.[12] (Found: Pb, 18·5; N, 10·3. Calc. for $Pb(C_{12}H_8N_2)_4(ClO_4)_2$: Pb, 18·4; N, 9·95%).

Bis-(1:10-*phenanthroline*)-*lead*(II) *perchlorate*. Prepared by heating the tetra-lead complex *in vacuo* at 185°. The loss in weight corresponded to two moles of phenanthroline per mole of starting complex. (Found: Pb, 26·9; N, 7·10. Calc. for $Pb(C_{12}H_8N_2)_2(ClO_4)_2$: Pb, 27·0; N, 7·30%).

Tris-(1:10-*phenanthroline*)-*bismuth*(III) *perchlorate*. Prepared by the method of PFEIFFER and CHRISTELEIT.[12] A colourless crystalline product was obtained after two recrystallizations from 1 per cent acetic acid. (Found: Bi, 19·3; N, 8·20. Calc for $Bi(C_{12}H_8N_2)_2(ClO_4)_3$: Bi, 19·9; N, 8·02%).

Tris-(1:10-*phenanthroline*)-*tin*(II) *perchlorate*. Preparation of this compound was attempted by the method reported in the literature[14] and various modifications. In all cases, the spectral results showed that no co-ordination to the metal had occurred and that the phenanthroline was present only as the perchlorate.

Tris-(2:2′-*bipyridine*)-*iron*(II) *perchlorate*, *tris*-(2:2′-*bipyridine*)-*iron*(III) *perchlorate trihydrate*, *tris*-(2:2′-*bipyridine*)-*cobalt*(II) *perchlorate*, *tris*-(2:2′-*bipyridine*)-*cobalt*(III) *perchlorate trihydrate* and *tris*-(2-2′-*bipyridine*)-*nickel*(II) *perchlorate*. These complexes were prepared according to the procedures given by BURSTALL and NYHOLM,[15] and their compositions confirmed by analysis.

Tris-(2:2′-*bipyridine*)-*manganese*(II) *perchlorate*. Prepared by adding a solution of 0·62 g bipyridine in 5 ml methanol to a solution of 0·17 g $MnSO_4 \cdot H_2O$ in 100 ml distilled water. The mixture was heated to effect solution, an excess of solid $NaClO_4$ added and the precipitate isolated after cooling to room temperature. Recrystallization from hot water yielded a bright yellow crystalline product. (Found: C, 50·1; H, 3·44; N, 11·7. Calc. for $Mn(C_{10}H_8N_2)_3(ClO_4)_2$: C, 49·9; H, 3·32; N, 11·6%).

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PREPARATION OF SOME BASIC AND ANHYDROUS RARE EARTH ACETATES. THEIR PROPERTIES AND REACTIONS IN ACETIC ACID AS SOLVENT

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Abstract—Solutions of rare earth oxides in anhydrous acetic acid represent metastable systems from which hydroxo-acetates, $Ln_2(OH)_3(OAc)_3 \cdot 2HOAc$, gradually precipitate. Presence of equivalent amounts of acetic anhydride causes formation of so-called basic acetates which are best represented as binuclear oxo- complexes with the type formula, $Ln_2O(OAc)_4 \cdot 2HOAc$ (where Ln = La, Nd, Sm). The anhydrous acetates were prepared by refluxing the oxides with acetic anhydride. The solubility of neodymium acetate in acetic acid increases markedly in the presence of potassium acetate to form a negatively charged complex ion, suggesting that the anhydrous rare earth acetates exhibit amphoteric characteristics in acetic acid. Conductometric titrations of solutions of the oxo- and anhydrous acetates in acetic acid with various acids show complete neutralization only with perchloric acid; with sulphuric and oxalic acids, minima correspond to formation of insoluble 1 : 1 compounds (moles acid per mole rare earth); with phosphoric and citric acids, maxima suggest formation of soluble 1 : 1 compounds, followed by minima corresponding to insoluble compounds with 3 : 2 and 2 : 1 mole ratios, respectively.

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THE marked solubility of neodymium oxide in anhydrous acetic acid, (HOAc), led to the hope that such solutions might find use for the preparation of anhydrous neodymium compounds. It was soon discovered that minor variations in the nature of the solvent produce a rather marked effect on the stabilities of such solutions. The pertinent observations may be summarized as follows:

(a) Solutions of the oxide in 98% HOAc (2% H_2O) are stable for many months, whereas solutions prepared using the anhydrous solvent gradually yield on standing at room temperature a precipitate whose composition can be represented by the formula, $Nd_2(OH)_3(OAc)_3 \cdot 2HOAc$.(I)

(b) Solutions of the oxide in 100% HOAc containing an amount of acetic anhydride, Ac_2O, stoicheiometrically equivalent to, or in excess of that required for removal of water presumably formed as the result of the solution process possess variable stability. If such systems are initially refluxed for several hours, formation of a crystalline precipitate begins to take place after several days. If the solutions have not been heated, precipitation will be delayed for a matter of weeks or even months. In both instances precipitation continues until only a small amount of neodymium remains in solution. These phenomena cannot be ascribed to supersaturation since seeding with crystals of the precipitated phase do not hasten formation of additional product. The precipitated compound, is found to correspond in composition to a hemihydrate, $Nd(OAc)_3 \cdot \frac{1}{2}H_2O$. For reasons given below and substantiated by the results of a study of the conductometric behaviour of such solutions and products, this compound is believed to be an oxo-acetate, $Nd_2O(OAc)_4 \cdot 2HOAc$(II). Similar binuclear oxo-acetates were obtained for La, Sm, Yt.

To further characterize the unusual nature of the products obtained from acetic acid–acetic anhydride solutions, it became necessary to prepare the anhydrous normal acetates. These were obtained by the interaction of acetic anhydride with the corresponding oxides (except for yttrium oxide, which was found to be non-reactive with Ac_2O). The anhydrous acetates were found to differ from the oxo-acetate(II) on the basis of:

(i) qualitative solubility differences in 100% HOAc,
(ii) their analytical compositions,
(iii) their X-ray diffraction patterns and
(iv) their reactions with various acidic solutions in 100% HOAc as solvent.

DISCUSSION OF RESULTS

Reaction of the rare earth oxides with solvent acetic acid

It is evident that the solutions of neodymium oxide in acetic acid are relatively metastable systems from which the hydroxo-, or the oxo-acetates, (I) and (II) slowly precipitate. The attack of the solvent upon the polymeric oxide structure can most certainly be regarded as a stepwise process entailing progressive cleavage of Nd–O–Nd linkages. Reactants in such systems include not only the *solvent*, but also *water*, which may have been present originally or formed during the solution or the subsequent stabilization processes. Where specified, *acetic anhydride* may also be considered to be a reactant. From a purely formalistic point of view, the following solvation reactions may be assumed to occur:

$$Nd_2O_3 + HOAc \rightarrow Nd_2O_2(OH)(OAc) \quad (A) \qquad (1)$$

$$A + HOAc \rightarrow Nd_2O(OH)_2(OAc)_2 \quad (B) \qquad (2)$$

$$B + HOAc \rightarrow Nd_2(OH)_3(OAc)_3 \quad (C) \qquad (3)$$

The solvolytic action of acetic acid upon any one of these hypothetical intermediates entailing replacement of hydroxo groups by acetato groups could also be important:

$$Nd_2O_{3-n}(OH)_n(OAc)_n + mHOAc \rightarrow Nd_2O_{3-n}(OH)_{n-m}(OAc)_{n+m} + mH_2O \qquad (4)$$

where $n,\ m = <3$

Equation (4) suggests that the presence of either water or of acetic anhydride could influence the nature of the species present in acetic acid or obtainable by precipitation from such systems. In any case such a picture leads to the conclusion that a binuclear complex may constitute the simplest structural unit obtainable as the intermediate or end product of the solution process. In the absence of acetic anhydride, a product represented by the general formula $Nd_2O_{3-n}(OH)_n(OAc)_n$ might therefore result from the solvation of neodymium oxide. A compound which may be represented by the formula for which $n = 3$ was actually isolated as a 2-acetic acid solvate (I). The presence of a small amount of water either retards formation of this substance or greatly increases its solubility as no crystalline products were obtained from a solution of Nd_2O_3 in 98 per cent acetic acid.

Attack of the intermediate hydroxo-compounds by the solvent acetic acid, entailing replacement of hydroxo-groups by acetato-groups should be favoured by the presence of acetic anhydride. The latter could serve not only to remove water formed during

the solvolytic process, but might also conceivably convert the hydroxo-bridged species into oxo-bridged complexes by a mechanism amounting to oxolation. It is our opinion that the processes of solvolysis (eqn. 5) and of oxolation (eqn. 6) represent the slow temperature-dependent reactions which lead eventually to the precipitation of the binuclear oxo-acetate(II) as the 2-acetic acid solvate.

$$Nd_2(OH)_3(OAc)_3 + HOAc \rightarrow Nd_2(OH)_2(OAc)_4 + H_2O \quad (5)$$

$$Nd_2(OH)_2(OAc)_4 + Ac_2O \rightarrow Nd_2O(OAc)_4 + 2HOAc \quad (6)$$

Even though the oxo-acetate(II) could be represented as a hemi-hydrate,

$$Nd(OAc)_3 \cdot \tfrac{1}{2}H_2O,$$

the dimeric structure with an oxo bridge is believed to be more reasonable, both on the basis of the mechanism outlined above, as well as the behaviour of this substance in acetic acid. The "basic" acetates of titanium[1] and of boron[2] are represented by similar structures. Basic acetates of chromium[3] have been assigned structures containing both oxo and acetato groups as bridging units.

The oxo-acetates(II) of neodymium, lanthanum, samarium, and yttrium were prepared, analysed and characterized during present investigation.

Interaction of rare earth compounds with acetic anhydride

Two procedures are given in the literature for the preparation of the anhydrous rare earth acetates: (a) the reaction of the rare earth nitrate 6-hydrate with acetic anhydride[4,5] and (b) the solution of the rare earth oxide in fused ammonium acetate.[6] Since the latter reaction is reported to give an impure product it was not further investigated. A critical evaluation of published results covering the first of these methods reveals that the analytical data correspond more satisfactorily with those rquired for the oxo-acetates. Analytical results for the La_2O_3 content of a so-called anhydrous lanthanum acetate bear out this contention (Found: 49·7 and 49·5. Calc. for $La(OAc)_3$; 51·6 and for $La_2O(OAc)_4 \cdot 2HOAc$, 50·2%). Investigators[4,5] who have most recently used this method did not perform elemental analyses.

Attempts in this laboratory to prepare the anhydrous acetates by refluxing the nitrates or the precipitated hydroxides with acetic anhydride gave only the oxo-acetates(II). Their formation was verified both by analsyis and by X-ray diffraction patterns. However, small samples of the oxo-acetates were found to undergo conversion into the anhydrous acetates when refluxed for approximately 16 hr with acetic anhydride. This suggests that reaction of the hydroxides or nitrates with acetic anhydride can lead to the formation of the anhydrous acetates if the reflux time is sufficiently long.

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Reaction of rare earth oxides with acetic anhydride

Reaction of neodymium oxide (and of La_2O_3 and Sm_2O_3) with boiling acetic anhydride yields the anhydrous acetate. A hydroxo compound cannot possibly be formed under these conditions. Here again the solvolysis of neodymium oxide may be regarded as entailing the stepwise destruction of the polymeric oxide structure. No solution appears to take place. Rupture of Nd–O–Nd linkages by simultaneous addition of the acetyl and acetate ions[7] presumably characterizing the reactive species formed by self-ionization of the solvent: $(CH_3CO)_2O \rightleftharpoons CH_3CO^+ + CH_3COO^-$ may constitute the principle mode of attack. Obviously incomplete reaction could result in the occlusion of oxide, or of the partially solvolysed material containing Nd–O–Nd units. The mechanism of the process can be represented formalistically in the following fashion:

$$[O\text{–}Nd\text{–}O\text{–}Nd\text{–}O]_n \xrightarrow{2n\,AcOAc} [(AcO)_2Nd\text{–}O\text{–}Nd(OAc)_2]_n \xrightarrow{n\,AcOAc} [Nd(OAc)_3]_n$$

Properties of the oxo- and anhydrous rare earth acetates

Both classes of acetates are soluble in water. The anhydrous acetates were more soluble in 100% HOAc than the basic acetates. The two classes of compounds were also found to differ with respect to their X-ray diffraction patterns and their I.R. spectra.

The visible and ultra-violet absorption spectra of the neodymium acetate in water and acetic acid, and of the metastable solutions of the oxide in acetic acid were found to reveal no significant differences. In general, the molar absorptivities of such solutions were found to be slightly lower in acetic acid than in water. The molar absorptivities of the three solutions at the 523 mμ absorption peak are given in Table 1. The observed value of 3·91 for neodymium acetate in water compares favourably

TABLE 1.—ABSORPTION OF VARIOUS NEODYMIUM ACETATE SOLUTIONS AT ca. 523 mμ

Compound	Solvent	Molar absorptivity
$Nd(OAc)_3$	Water	3·91
$Nd(OAc)_3$	Acetic acid	3·61
Nd_2O_3–HOAc solution	Acetic acid	3·53

with the figure given in the literature, 3·80.[8] The results of this spectrophotometric study verify the near constancy of the absorption spectra of the neodymium compounds. Slight differences have been observed in different solvents and with different anions, but no marked changes in absorption spectra have been observed except in the case of very strong complexing action.

Amphoterism of neodymium acetate. The solubility of anhydrous neodymium acetate in acetic acid was found to increase upon the addition of potassium acetate. Data are given in Table 2. Migration experiments showed that the coloured solutions move toward the positive electrode indicating the formation of a negatively charged

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ionic species containing an acetato–neodymiate(III) complex. These observations may be interpreted by the following general equation:

$$Nd(OAc)_3 + nKOAc \rightarrow K_n[Nd(OAc)_{3+n}]$$

Neodymium acetate may thus be added to the list of inorganic acetates that exhibit amphoteric behaviour in acetic acid. It seems most likely that other rare earth acetates will show similar behaviour.

TABLE 2.—SOLUBILITY OF NEODYMIUM ACETATE IN ACETIC ACID AS A FUNCTION OF ACETATE CONCENTRATION (temp. 30°C)

Solubility g $Nd(OAc)_3$/100 g HOAc	KOAc concentration molarity
1·94	0·00
2·00	0·10
4·25	0·50
7·26	1·00

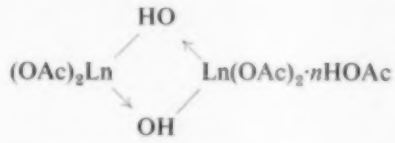
Reactions of rare earth oxide solutions in acetic acid with various acids. The present investigation was undertaken in order to study the practicability of preparing anhydrous rare earth compounds from solutions of the oxides in acetic acid. Analytical results for products obtained by the addition of various acids to the rare earth oxide–acetic acid solutions were found to be difficult to interpret. Conductometric titrations were therefore carried out to gain a clearer insight into the nature of these reactions. Surprisingly, the titation curves for solutions of the oxides and of the anhydrous acetates in acetic acid were found to reveal no significant differences in form or shape. The titration curves are plotted schematically in Fig. 1 in terms of moles acid per mole Nd. Similar curves were obtained for solutions of the corresponding lanthanum and samarium compounds.

The complete "neutralization" of the rare earth species with perchloric acid is indicated by a break in the titration curve at a molar ratio of 3 : 1 for $HClO_4$: Nd. For H_2SO_4, $H_2C_2O_4$, citric acid and phosphoric acid 1 : 1 compounds are suggested. The 1 : 1 reaction products with sulphuric and oxalic acid are precipitated completely, whereas those formed with citric acid and phosphoric acid appear to be appreciably soluble. However, precipitation of a citrate with a 2 : 1 molar ratio (citric acid : Nd) begins beyond the maximum of the conductance curve and of a 3 : 2 compound with phosphoric acid begins to occur just before the maximum is reached. Since all titration curves show initial increases in conductance whether precipitation takes place or not, there is some question whether the pronounced maxima at the 1 : 1 ratios, obtained when solutions of citric and phosphoric acids were used as titrants, represent soluble compounds corresponding to this ratio.

Only when perchloric acid, one of the strongest acids known to exist in acetic acid, was used as the titrant does the conductometric evidence suggest complete reaction. Results obtained for the other acids suggest that only two of the three acetate groups per neodymium atom in the oxo- and anhydrous acetates, when formulated as $Nd(OAc)_3 \cdot \frac{1}{2}H_2O$ and $Nd(OAc)_3$, respectively, participate in the reaction.

The conductometric evidence together with the analytical data for the oxo- and anhydrous acetates therefore demonstrate

(a) that solutions of the oxides in acetic acid can be represented in their simplest form as binuclear hydroxo-acetates:

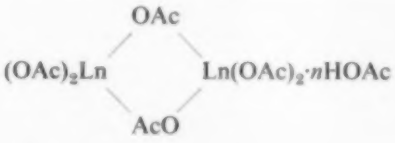


(b) that the oxo-acetates formed by gradual crystallization from such solutions containing acetic anhydride can be considered as oxolated complexes:

$$(OAc)_2Ln\text{–}O\text{–}Ln(OAc)_2 \cdot n HOAc$$

and

(c) that even the anhydrous acetates behave in acetic acid as polymeric species in which acetato-groups constitute bridging units, as follows:



For purposes of comparison conductometric titrations were also carried out using solutions of potassium acid phthalate with the same acids. Solvolysis of potassium acid phthalate to give potassium acetate and the non-electrolyte, phthalic acid, makes it possible to use the phthalate as a base standard in HOAc.[9] The titration data are plotted schematically in Fig. 2 and show

(a) that perchloric acid and phosphoric acid serve as mono-basic acids to form $KClO_4$ and KH_2PO_4, respectively,

(b) that sulphuric acid yields both the normal as well as the hydrogen sulphates, K_2SO_4 and $KHSO_4$, and

(c) that oxalic and citric acids are non-electrolytes in acetic acid.

EXPERIMENTAL

Materials and methods

(a) *Anhydrous acetic acid.* Preparation of the anhydrous solvent from glacial acetic acid was effected by two procedures:

(1) by refluxing the 99·7 per cent acid with CrO_3 to remove oxidizable impurities followed by treatment with "boron acetate" to effect removal of water[10] and

(2) by dehydration with acetic anhydride.[11] Refluxing of the acid with the anhydride (500 ml CH_3COOH plus 15 ml $(CH_3CO)_2O$) for 3 hr is reported to effect quantitative reaction between the anhydride and water present in acetic acid. Final purification was accomplished in both instances by fractional distillation.

(b) *Rare earth materials.* The neodymium oxide used in this investigation was material of 99·9 per cent purity taken from the University of Illinois stock. The yttrium, samarium and lanthanum

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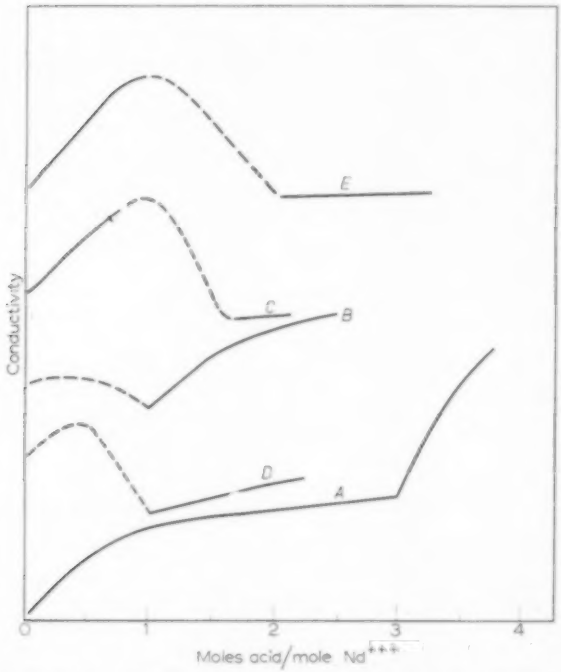

FIG. 1.—Conductometric titration curves representing addition of various acids to solutions of neodymium oxide (or of the acetate or oxo-acetate) in 100% HOAc. Broken lines indicate formation of precipitates. Titrants: *A*, 0·1 M/$HClO_4$; *B*, 0·05 M/H_2SO_4; *C*, 0·4 M/H_3PO_4; *D*, 0·1 M/$H_2C_2O_4$; *E*, 0·1 M citric acid. $[Nd^{3+}] = \sim 0{\cdot}01$ M.

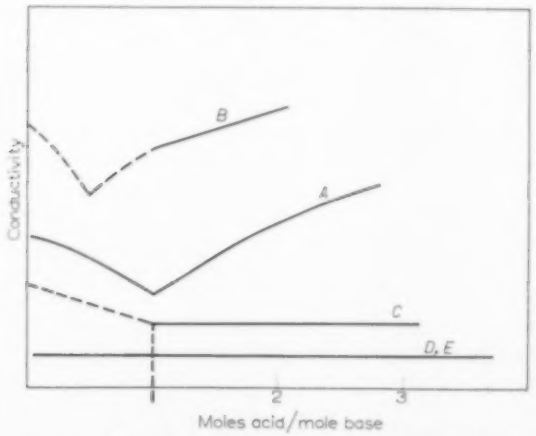

FIG. 2.—Schematic presentation of conductometric titration curves of potassium hydrogen phthalate as base standard in 100% HOAc using various acids. Solutions contained about 0·2 g KHPhth per 150 ml HOAc as solvent. Titrants: *A*, 0·1 M/$HClO_4$; *B*, 0·05 M/H_2SO_4; *C*, 0·4 M/H_3PO_4; *D* and *E*, $H_2C_2O_4$ and citric acid. Broken lines indicate precipitate formation ($KHSO_4$, K_2SO_4, KH_2PO_4). Solutions of oxalic and citric acids are essentially non-acidic in 100% HOAc.

oxides (purity "99 per cent plus") were obtained from the Lindsay Chemical Company. The oxides were ignited at 800–900° before use.

The hydrated neodymium and yttrium hydroxides were prepared by the addition of ammonium hydroxide to solutions containing their respective nitrates. The hydroxides were washed with water, ethanol and ether, and dried for 6 hr at 106°C.

(c) *Experimental techniques.* Conductometric titrations were carried out utilizing a Leeds and Northrup bridge, Model 4866. The electrodes consisted of 1 cm^2 platinum sheets separated from each other by a distance of 2 mm. Titrations were carried out at 25–26° and at 30°.

Spectrophotometric measurements in the ultra-violet and visible regions were determined by use of a Cary Model 14 M recording spectrophotometer. A Perkin–Elmer Model 21 instrument was employed for the infra-red studies. One centimeter quartz cells were used with the Cary spectrophotometer; nujol mulls were prepared for use with the Perkin–Elmer instrument. The infra-red spectra were used only for purposes of comparison.

X-ray powder patterns were obtained by use of a Hull-Debye-Scherrer X-ray diffraction apparatus equipped with a copper target and utilizing a nickel filter. The samples were sealed in Lindeman glass tubes. The X-ray diffraction patterns were employed only for purposes of comparison and identification.

(d) *Analytical methods.* The carbon and hydrogen contents of the various rare earth compounds were determined by standard microanalytical methods. Final ignition of microanalytical samples was accomplished by heating at 950°C for approximately 10 min. The resulting residues were also weighed to give values for the rare earth oxide contents of the samples. These values compared favourably with results obtained when macro samples were dissolved in nitric acid and treated with oxalic acid solution to precipitate the rare earth oxalates. The oxalates were subsequently ignited to the oxides.

(e) *Standard solutions in* 100% CH_3COOH. The titres of solutions were checked conductometrically against potassium acid phthalate which serves as a primary base standard in acetic acid.

Standard solutions of sulphuric acid (0·05 M) and of phosphoric acid (0·4 N) were prepared from 95 to 98% H_2SO_4 and 85% H_3PO_4, respectively, by dissolving weighed quantities of each in acetic acid, adding the calculated quantity of acetic anhydride to remove water introduced with the acids refluxing briefly to effect reaction between the anhydride and water, and diluting to known volumes. Such solutions were allowed to stand for two days before use.

Solutions of oxalic acid in acetic acid prepared by dissolving the 2-hydrate were found to decompose rapidly with gas evolution when acetic anhydride was added to effect removal of water. It was therefore necessary to prepare standard solutions from anhydrous oxalic acid (furnished by the Victor Chemical Works). Solutions containing approximately 0·1 mole oxalic acid per litre were prepared by dissolving accurately weighed samples in acetic acid.

Tenth molar solutions of citric acid were prepared by dissolving accurately weighed samples of the 1-hydrate in anhydrous acetic acid containing the calculated amount of acetic anhydride to react with the water present. The solution was diluted to a known volume with anhydrous solvent and allowed to stand two days before use. Some evidence for decomposition was observed after standing for one week, based upon variable titrimetric results against standardized neodymium solutions.

Interaction of rare earth oxides with acetic acid

(a) *In the presence of acetic anhydride (formation of the oxo-acetates).* Solutions of rare earth oxides in acetic acid were prepared by dissolving weighed portions of the ignited oxides in acetic acid and refluxing the solutions for 3 hr with an amount of acetic anhydride calculated to remove the water formed on the assumption that the reaction would produce the anhydrous acetates. Yttrium oxide was found to be insoluble and unreactive. The solutions were cooled and diluted to known volumes with anhydrous acetic acid and the molarities of the solutions calculated with respect to the rare earth ion contents. Solutions in which as much as 4 g of the oxide were dissolved in 100 ml of acetic acid were prepared in this manner. Such solutions were used directly for conductometric studies and for the preparation of the oxo-acetates.

Neodymium solutions were found to yield precipitates after standing at room temperature for five days or longer (up to several months in those instances where the solutions had not been refluxed). Attempts to seed solutions with crystals of the precipitate were unsuccessful. Precipitation was observed to take place more rapidly from solutions of the samarium and the lanthanum oxides.

The precipitates were found to be the same whether a calculated or a two-fold excess of acetic anhydride had been added to react with the water assumed to be formed. The crystalline compounds were dried over calcium chloride and potassium hydroxide in a vacuum desiccator for ten days after which the odour of acetic acid was no longer evident and the compositions as determined by analysis had become constant. Compounds of the same composition were obtained by drying the crystalline substances for 24 hr in an Abderhalden apparatus at 100°C. Typical analyses for the compounds which are designated as *oxo-acetates* are given below:

Found: C, 22·00; H, 2·78; La, 42·75. Calc. for $La(OAc)_3 \cdot \frac{1}{2}H_2O$: C, 22·17; H, 3·11; La, 42·73%. Found: C, 21·70; H, 3·06; Nd, 43·6. Calc. for $Nd(OAc)_3 \cdot \frac{1}{2}H_2O$: C, 21·82; H, 3·05; Nd, 43·66%. Found: C, 21·60; H, 3·13; Sm, 45·5. Calc. for $Sm(OAc)_3 \cdot \frac{1}{2}H_2O$: C, 21·47; H, 2·99; Sm, 44·7%.

The oxo-acetates were found to be soluble in water, but insoluble in ethanol, nitrobenzene, benzene, diethyl ether, and acetone. The oxo-acetates can be recrystallized from anhydrous acetic acid. These substances are believed to be binuclear oxo complexes, and may be represented by the type formula, $Ln_2O(OAc)_4 \cdot 2HOAc$ (where Ln = lanthanon).

(b) *In the absence of acetic anhydride (formation of hydroxo-acetates).* One gramme of ignited neodymium oxide was dissolved by refluxing for 1 hr in 25 ml of anhydrous acetic acid. The precipitate which formed after approximately one week was dried for two days on a porous plate in a vacuum desiccator over potassium hydroxide and calcium chloride. The sample was then dried in an Abderhalden apparatus at 100°C for 24 hr. Found: C, 18·49; H, 2·85; Nd, 45·6. Calc. for $Nd_2(OH)_2(OAc)_2 \cdot 2HOAc$: C, 18·85; H, 3·16; Nd, 45·32%).

Interaction of rare earth compounds with acetic anhydride

Anhydrous rare earth acetates were obtained when the oxides of lanthanum, neodymium and samarium were refluxed with acetic anhydride; the oxo-acetates were formed when neodymium and yttrium hydroxides and neodymium nitrate 6-hydrate were allowed to react with acetic anhydride.

(a) *Rare earth hydroxides.* Approximately 2·5 g of hydrated neodymium hydroxide was refluxed for 3 hr with 100 ml of acetic anhydride. No solution appeared to take place, but the product changed in appearance as refluxing was continued. The resulting compound was dried on a porous plate in a vacuum desiccator over potassium hydroxide and calcium chloride for two days and then dried for 24 hr in an Abderhalden apparatus at 100°C. The X-ray diffraction pattern revealed the compound to be the oxo-acetate.

Found: C, 21·64; H, 3·00; Nd, 43·7. Calc. for $Nd(OAc)_3 \cdot \frac{1}{2}H_2O$: C, 21·82; H, 3·05; Nd 43·66%).

(b) *Rare earth nitrates.* Approximately 4 g of neodymium nitrate 6-hydrate was dissolved in 25 ml of acetic anhydride. The solution was heated gently until reaction occurred with the evolution of nitrogen dioxide and the concurrent formation of a very viscous substance. The product gradually hardened; heating was continued until no more nitrogen dioxide was evolved. The precipitate was crushed, washed with acetic anhydride, and dried on a porous plate in the vacuum desiccator over potassium hydroxide and calcium chloride for two days, followed by an additional 24 hr in an Abderhalden apparatus at 100°C. The diffraction pattern of this product was found to agree with that of the oxo-acetate.

Found: C, 20·77; H, 2·85; Nd, 43·2. Calc. for $Nd(OAc)_3 \cdot \frac{1}{2}H_2O$: C, 21·82; H, 3·05; Nd, 43·66%).

(c) *Rare earth oxides.* Four grammes of ignited neodymium oxide was refluxed with 200 ml of acetic anhydride. A light blue suspension was formed which turned violet in colour upon applying heat. The suspension cleared when the refluxing became vigorous; the rare earth compound settled to the bottom of the flask as a viscous mass which quickly formed a hard cake. After 2 hr of refluxing, the solid mass was broken up thoroughly and refluxing continued for 4–8 hr. Samples of La_2O_3 and Sm_2O_3 were treated in a similar fashion. Yttrium oxide was found to be unreactive. Products after drying were found to give analytical results demonstrating that the anhydrous acetates had been formed.

Found: C, 22·63; H, 2·98; La, 44·4. Calc. for $La(OAc)_3$: C, 22·80; H, 2·87; La, 43·96%.
Found: C, 22·19; H, 2·98; Nd, 44·9. Calc. for $Nd(OAc)_3$: C, 22·42; H, 2·82; Nd, 44·89%.
Found: C, 21·59; H, 2·99; Sm, 46·0. Calc. for $Sm(OAc)_3$: C, 21·99; H, 2·77; Sm, 45·93%.

These compounds were found to be completely soluble in water and anhydrous acetic acid. The

X-ray diffraction patterns of these compounds were found to be different from those of the oxo-acetates. The anhydrous acetates are believed to be poly-nuclear (in acetic acid) with bridging acetato groups (see page 227).

(d) *Neodymium oxo-acetate*. One gramme of the oxo-acetate of neodymium was refluxed with 50 ml of acetic anhydride for approximately 16 hr. The sample was removed and dried first in a vacuum desiccator for two days over potassium hydroxide and calcium chloride and subsequently in the Abderhalden for 24 hrs at 100°C. The X-ray diffraction pattern of the product prepared in this manner was found to be identical with that of the anhydrous acetate:

Found: C, 22·31; H, 2·87; Nd, 44·8. Calc. for $Nd(OAc)_3$: C, 22·42; H, 2·82; Nd, 44·89%. The above experiment suggests that long refluxing of the oxo-acetates with acetic anhydride will effect their conversion to the anhydrous acetates.

Acknowledgements—The authors are indebted to the Atomic Energy Commission for a grant in support of this investigation (Contract No. AT(11-1)-67, Project No. 18). Some of the earlier exploratory work on this problem was carried out by Mr. R. E. Whitney (B.S. Thesis, University of Illinois, 1955) whose efforts are acknowledged with gratitude. The authors are also grateful to Mr. J. Nemeth for the microanalytical determinations and to Professor G. T. Moeller for helpful suggestions.

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THE THERMAL DECOMPOSITION OF IRRADIATED SILVER PERMANGANATE

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Abstract—The thermal decomposition of $AgMnO_4$, pre-irradiated in BEPO and in a ^{60}Co γ-'hot spot', has been investigated in the temperature range 100–125°C. The results are similar to those for irradiated $KMnO_4$ and the mechanism proposed for the latter is again suggested. The activation energy for the migration of point defects over the induction period is 1·09 eV. The decomposition of unirradiated and irradiated crystals differ in that the latter undergo physical disintegration over the acceleratory period. X-ray studies immediately prior to disintegration show strain and fragmentation in the irradiated crystal. An explanation is advanced for the changes produced in the p/t plots with increased dosage, and a fixed decomposition temperature.

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THE thermal decomposition of solid $KMnO_4$ *in vacuo* is markedly affected by pre-irradiation with thermal neutrons, γ-rays (1·3 MeV), and protons (145 MeV). The effects are in accordance with a suggested mechanism involving the annealing of point defects.[1] The acceleration of the reaction at the end of the induction period is considered to be due to the physical break-up of the solid caused by the strain engendered in the crystal by the presence of decomposition spikes. The thermal decomposition of small whole and ground silver permanganate crystals was previously investigated in the temperature range 105–120°C.[2] The decomposition of whole $AgMnO_4$ crystals is similar to that of single crystals of $KMnO_4$; the p/t plot is sigmoid and exhibits an induction period; grinding shortens the induction period, while pre-irradiation with ultra-violet light or cathode rays has no measurable effects on the decomposition. However, the decompositions differ in that the small whole crystals of $AgMnO_4$ show no physical fracturing throughout the entire decomposition, and the induction period is accompanied by the slow evolution of gas. Interesting effects were thus to be expected by irradiating $AgMnO_4$ with thermal neutrons and γ-rays.

EXPERIMENTAL

The preparation of the small $AgMnO_4$ crystals (0·3 × 0·03 mm), the apparatus, and the procedure used were as as previously described.[2] Large crystals of $AgMnO_4$ (4·0 × 0·5 mm) were formed from a saturated aqueous solution of $AgMnO_4$ maintained for 24 hr at 40°C in a vacuum oven.

Pile irradiations were performed in BEPO in a position near the outside. The specimens were sealed in silica ampoules and exposed to a thermal neutron flux of 2×10^{7} neutrons cm^{-2} sec^{-1} at an ambient temperature of 30 ± 5°C. Irradiations in the thermal column of BEPO with a flux of 7×10^{9} neutrons cm^{-2} sec^{-1}, were carried out for 168 hr on specimens enclosed in A.R.Pb containers. γ-Ray irradiations were carried out, at room temperature, in a ^{60}Co "hot-spot" of total activity 439 curies. The dose rate, as measured by ferrous–ferric methods, was $1·6 \times 10^{6}$ r.e.p. hr^{-1}. ^{60}Co emits γ-rays of 1·33 and 1·17 MeV.

Unless otherwise stated, the whole and ground crystals weighed 20 ± 3 mg. Normalization to a common pressure was done for comparative purposes.

[1] E. G. PROUT, *J. Inorg. Nucl. Chem.* **7**, 368 (1958).
[2] E. G. PROUT and F. C. TOMPKINS, *Trans. Faraday Soc.* **42**, 468 (1946).

RESULTS

Pre-irradiation of whole $AgMnO_4$ crystals for 15 hr in either BEPO or the γ-hot-spot gave, for a particular irradiation, highly reproducible p/t plots. With ground crystals, the results were not as satisfactory.

There was no mass effect. Fig. 1 illustrates the effects of pile and γ-ray irradiations on whole and ground specimens.

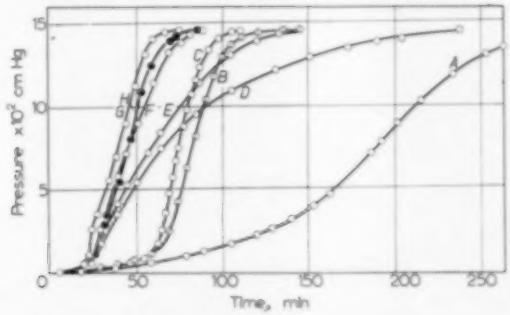

FIG. 1.—Effect of pre-irradiation on the thermal decomposition of whole and ground crystals at 105°C.
A–unirradiated whole crystals; *B*–whole crystals, 163 hr γ; *C*–whole crystals, 15 hr pile; *D*–unirradiated ground crystals; *E*–ground crystals, 6 hr γ; *F*–ground crystals, 48 hr γ; *G*–ground crystals, 2 weeks γ; *H*–ground crystals, 48 hr pile.

Visual observation during decomposition at 115°C of 20 mg of small unirradiated whole crystals, and a single unirradiated whole crystal (6 mg) showed that neither specimen underwent any physical disintegration. The single crystal retained its external crystal morphology to the completion of the reaction. Specimens pre-irradiated in the pile or hot-spot, however, showed no splintering over the induction period but began to disintegrate at the commencement of the acceleratory period, and the disintegration continued until the commencement of the decay period. The degree of disintegration with 48 hr pre-irradiation was considerably greater than with 2 hr pre-irradiation. The time at which physical fracture began in the decomposition of γ-irradiated and pile-irradiated whole crystals was assumed to mark the end of the induction period. This time in the case of both small and large whole crystals coincided with the intercept on the time axis made by the tangent at the point of maximum velocity.

Decomposition of small whole crystals at 105°C after various times of γ-irradiation are illustrated in Fig. 2. Similar results were obtained for pile irradiation of small whole crystals. The variation of the length of the induction period with dosage (at a fixed decomposition temperature) was found to obey the equation log (time of irradiation) $= kI + c$; where $I =$ the length of the induction period. The results for whole crystals are shown in Fig. 3.

The effect of interrupting the decomposition of unirradiated whole crystals after a definite time, irradiating in the γ-hot-spot for a constant time, and then continuing the decomposition to completion was studied as before. The results for large crystals decomposed at 115°C and with a γ-irradiation time of 21 hr are shown in Fig. 4. Similar results were obtained for γ-irradiated small crystal specimens.

The possibility of an experimentally measurable quantity of gas being produced,

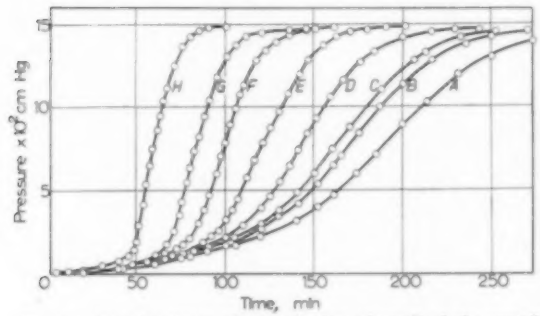

FIG. 2.—Varying times of γ-irradiation of small whole crystals; decomposition temperature 105°C.
Time of γ-irradiation: *A*–0 min; *B*–5 min; *C*–10 min; *D*–30 min; *E*–2 hr; *F*–6 hr; *G*–16·3 hr; *H*–64·8 hr.

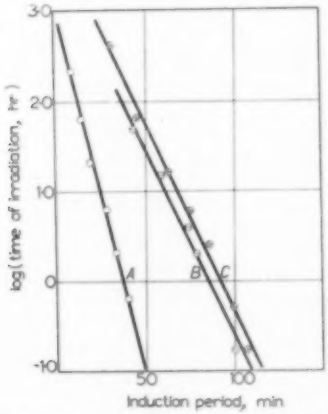

FIG. 3.—Relation between induction period and irradiation time.
A-large crystals, γ-irradiated, decomposed at 115°C; *B*–small crystals, pile-irradiated, decomposed at 105°C; *C*–small crystals, γ-irradiated, decomposed at 105°C.

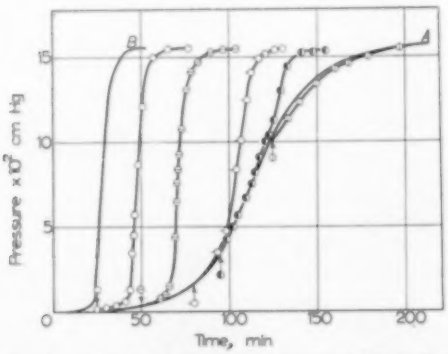

FIG. 4.—Curves showing effect of interrupting a decomposition at time shown by appropriate arrow, irradiating for 21 hr in γ-hot-spot, and then continuing decomposition with original $t = 0$ min. Times of interruption as indicated by arrows:
A-uninterrupted; *B*–0 min; ○–25 min; ⊖–50 min; ⊙–80 min; –◐ 110 min; ⓘ–125 min

and trapped in the crystal(s) over the induction period, was examined. Accurately weighed, irradiated single and small whole crystals were decomposed in a Pyrex glass bucket, the decomposition then interrupted, the crystal ground in the bucket using a short Pyrex rod (subsequently left in the bucket), the bucket returned to the high

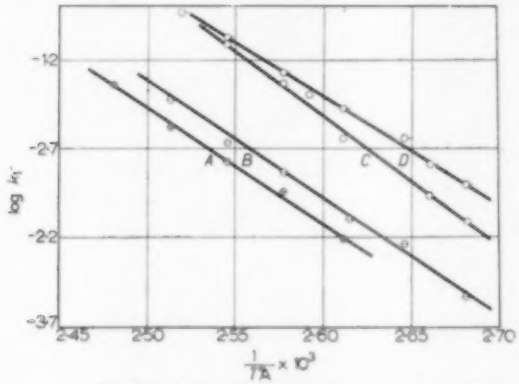

FIG. 5.—Activation energies for decay period.
A–unirradiated large crystals; *B*–unirradiated small crystals; *C*–small crystals: 6 hr γ-irradiation; *D*–small crystals: 15 hr pile-irradiation.

vacuum system and the run continued. The final pressure was determined and compared with that for an uninterrupted decomposition (after a mass correction). The results showed that no significant volume of gas was trapped either during, or at the end of the induction period.

The decomposition curves for unirradiated ground and whole $AgMnO_4$ crystals were previously found to follow the Prout–Tompkins equation

$$\log [p/(p_f - p)] = k_1 t + c \tag{2}$$

over the acceleratory region. The equation

$$\log (p_f - p) = k_2 t + c \tag{3}$$

gave a better fit over the decay than equation (2).[2] Both these equations fitted the p/t plots of pile and γ-irradiated whole crystals over the whole of the decay period. Activation energies over the decay period were calculated using equation (2). The plots $\log k_1$ vs. $(1/T)$ are shown in Fig. 5. The activation energies calculated from the plots are tabulated in Table 1.

TABLE 1

Specimen	E_1 (kcal mole^{-1})
Small crystals unirradiated[3]	29·6
Small crystals unirradiated	28·8
Small crystals 15 hr pile	27·9
Small crystals 6 hr γ	33·3
Small crystals 2 weeks γ	31·3

Activation energies were also calculated from the plot log $(1/I)$ vs. $(1/T)$ for irradiated specimens. (Fig. 6). The results are tabulated in Table 2.

The decomposition, after irradiation in the thermal column, showed, as in the case of $KMnO_4$ that the effect produced was similar to that caused by an irradiation in the usual position in BEPO.

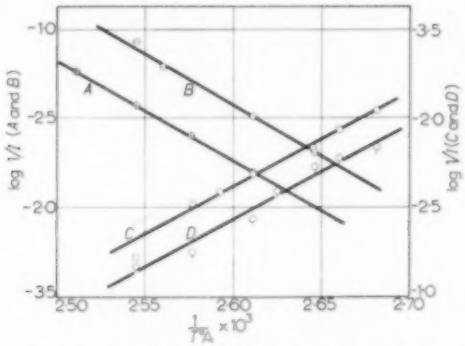

FIG. 6.—Activation energies for induction period.
A–large crystals: 38 min γ; *B*–large crystals: 220 hr γ; *C*–small crystals: 6 hr γ;
D–small crystals: 15 hr pile.

The decomposition of ground irradiated material (Fig. 1) showed a saturation effect as with $KMnO_4$. Visual observation showed that even the small particles underwent violent physical disintegration at the onset of acceleration and the conclusions drawn from the study of irradiated ground $KMnO_4$ appear valid here.

TABLE 2

Specimen	Activation energy (eV)
Small crystals 6 hr γ	1·07
Small crystals 15 hr BEPO	1·03
Large crystals 38 min γ	1·15
Large crystals 220 hr γ	1·10

An X-ray study of the solid at various stages of decomposition was made. Oscillation, zero, and first layer Weisenberg photographs using filtered Cu radiation were taken about the needle axis of a single unirradiated crystal [100]. The cell dimensions were in good agreement with those obtained by SASVARI.[3] Since grinding has a marked effect on the rate of thermal decomposition, diffractometer traces were made for a lightly and a heavily ground sample in order to determine the effects of grinding on the quality of the crystals. The results showed only very slight peak broadening even for the sample which was heavily ground for 1 hr in a mechanical mortar, proving that this treatment does not destroy the crystallinity.

Laue photographs were taken using unfiltered Mo radiation and proved to be the most sensitive way of detecting changes produced on heating. Photographs of single

[3] K. SASVARI, *Z. Krist.* **99**, 9 (1938.)

unirradiated crystals mounted about the [100] axis were taken after varying times of decomposition at 115°C (Fig. 7, Curve *A*;). During the induction period the spots remained fairly sharp though there was an increase in general diffuse scattering and in thermal scattering. After 68 min a symmetrical diffuse ring in the region $(\sin\theta)/\lambda \approx 0{\cdot}18$ Å^{-1} appeared and there were indications of internal strain. After 105 min a second ring appeared in the region $(\sin\theta)/\lambda \approx 0{\cdot}33$Å^{-1}. As the reaction proceeded

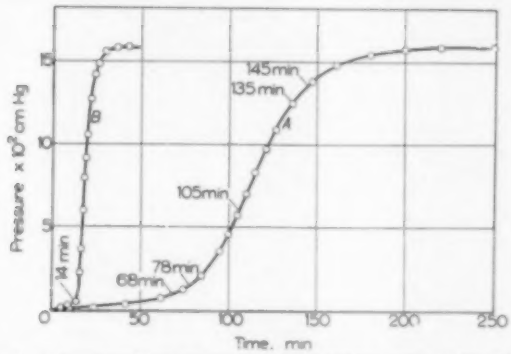

FIG. 7.—Decomposition curves for X-ray studies, temperature 115°C.
A–large crystals: unirradiated; *B*–large crystals: 220 hr γ.

the intensities of the diffuse rings increased while the crystalline spots were gradually reduced in the high angle region. Even after 135 min the spots were still present but after 145 min they had completely vanished, and two rings remained. This position was unchanged throughout the remaining decomposition.

The surface decomposition of large unirradiated crystals was also examined. Crystals decomposed for only 5 min at 115°C were immersed in water for 1 hr without the appearance of the characteristic permanganate colour. Undecomposed crystals from the same preparation coloured the water within 10 sec. The partially decomposed crystal, when broken under water, rapidly coloured the water from the newly exposed surfaces. Similar results were obtained for crystals decomposed for 13 min and 78 min, indicating in all cases the formation of a sheath of product around the crystal. Using Cu radiation, oscillation spots were visible on an X-ray photograph of material decomposed for 78 min, indicating that the product sheath must be less than 0·01 mm thick. Laue photographs of two interior fragments showed crystallinity spots and the diffuse ring.

Laue and Weisenberg photographs were taken of an undecomposed crystal which has been irradiated for 220 hr by γ-rays. The Weisenberg photographs were identical with those of unirradiated undecomposed crystals. The Laue photograph was similar to that of the unirradiated, undecomposed crystal except that there was more thermal and diffuse scattering. Laue photographs of the same irradiated crystals decomposed for 14 min at 115°C (Fig. 7, curve *B*) showed broken up spots, considerable asterism, and faint extra spots due to fragmentation of the crystal. Laue photographs of irradiated and unirradiated crystals after complete decomposition were identical.

DISCUSSION

The results obtained with irradiated ground and whole crystals are in general agreement with those found for $KMnO_4$. It is probable that the displacement of

Ag^+ ions into interstitial positions is caused mainly by recoil from the photoelectric effect. The photoelectrons will produce further displacements but the total number of secondary displacements will not be greatly in excess of the number of photoelectrons, since the threshold radiation energy for displacement of atoms of atomic weight 100 by electrons is 0·68 MeV (assuming the Seitz value of 25 eV). The knocked-on atoms will seldom have sufficient energy to produce secondaries.

It is assumed, as before, that over the induction period the point defects anneal out, and that the energy released at the site of recombination of the interstitial and vacancy causes the formation of a centre of decomposed material, and that this grows, due to the lowered activation energy for vacancy jump around it, to produce a decomposition spike. It should be stressed here that the undecomposed material is already at its decomposition temperature when the energy is released. The activation energies obtained from the plot log $(1/I)$ vs. $(1/T)$ indicate the migration of vacancies and the results are in agreement with those for $KMnO_4$.

Decomposition spikes will be formed along dislocation lines since their initial formation is favoured at such sites. Strain will thus be produced along the dislocation lines and fracture will probably originate in these regions. This view is supported by the X-ray results, which indicate distortion and fragmentation of the lattice at the end of the induction period. The absence of fracturing in unirradiated material and failure to detect any accumulated gas in the irradiated crystal immediately prior to disintegration, show that free escape of liberated gas from the solid occurs. The strain within the irradiated crystal is thus produced by the solid product.

The failure to observe any real difference in the Weissenberg X-ray photographs of γ-irradiated and unirradiated undecomposed material may be explained on the grounds that the lattice expansion caused by the displacement of atoms may be too small to detect. PRIMAK *et al.*[4] found that with a fast neutron dose of 5×10^{20} neutrons cm^{-2} there were no detectable changes in the X-ray photographs of beryl, GeO_2, Ge, Si, corundum (Al_2O_3) and rutile (TiO_2), whereas there were observable lattice expansions of about 0·1 per cent in MgO, spinel and CaF_2, and of 1 per cent in diamond and silica carbide.

As with $KMnO_4$ the results illustrated in Fig. 4 indicate that different types of nuclei operate in unirradiated and irradiated material. Decomposition of unirradiated material is assumed to occur along small cracks "perpendicular" to planes of decomposition.[2] Evidently the product is able to accommodate itself in the space available in the cracks without fracturing the crystal. The onset of fracturing with irradiated crystals always occurs at a pressure above that given by the unirradiated decomposition at the same time, indicating the formation of product molecules additional to those produced by the "normal decomposition". The former, as already suggested, are favourably placed for crystal fracture.

The initial decomposition of a fragment resulting from fracture is considered to consist of the rapid spread of the reaction over the newly formed surface. This is followed by the inward progression of the reactant–product interface. The mechanism of this progression is assumed to be that previously postulated for the decomposition of unirradiated $KMnO_4$.[5]

The effects of increased dosage, with a fixed decomposition temperature, are (a) a

[4] W. PRIMAK, *Phys. Rev.* **95**, 837 (1954); W. PRIMAK, L. H. FUCHS and P. DAY, *Ibid.* **92**, 1064 (1953).
[5] E. G. PROUT and F. C. TOMPKINS, *Trans. Faraday Soc.* **40**, 488 (1944).

shortening of the induction period, (b) an increase in the maximum velocity to a limiting value, (c) a decrease in the duration of the decay period and, (d) after the attainment of the saturation velocity, a decrease in the pressure at the onset of decay. The shortening of the induction period is due to an increase in the density of point defects with a consequent decrease in the time required for the strain to attain a critical value. The degree of disintegration should increase with dosage since with the greater density of defects a larger number of the dislocations in the crystal will contribute to fracturing. The changes in the maximum velocity and decay time can be attributed to the increased surface area of the solid. The degree of disintegration, and thus the maximum velocity, is expected to reach a limiting value dependent on the density of the crystal dislocations. The reaction during the period of fracture will involve in addition to the acceleratory surface reaction, the decay reaction of particles produced in the early stages. Irradiation times greater than that giving rise to the limiting velocity will cause a shortening of the period of fracture, as explained for irradiated $KMnO_4$. This will lower the pressure at the end of the fracture period since there will be a decrease in the extent of the decay reaction of fragments formed during fracture.

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CONCLUSIONS

The effects of irradiation by γ-rays and thermal neutrons on the subsequent thermal decomposition of $AgMnO_4$ are similar to those for $KMnO_4$. This work, however, shows the importance of the solid product in producing strain within the crystal structure. X-ray studies have yielded results which support the suggested nucleation mechanism over the induction period. The activation energy for this process has been determined.

The effect of pre-irradiation on the thermal decomposition of $KMnO_4$ and $AgMnO_4$ suggest that decomposition spikes, are formed during the induction period. Decomposition spikes, however, may possibly be formed during irradiation by fast neutrons as a result of the creation of thermal and/or displacement spikes. The decomposition of caesium and rubidium permanganates is being investigated with this possibliity in view. The temperatures of decomposition of these substances allow irradiation in hollow slugs in BEPO.

Acknowledgements—The authors wish to thank the C.S.I.R.(S.A.) for a grant to cover the cost of irradiations, and for a scholarship held by one of us (M. J. S.) during the investigation. Thanks are also due to Dr. F. H. Herbstein of the C.S.I.R. for his assistance in the X-ray studies.

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THERMAL ANNEALING OF RECOIL ARSENIC ATOMS IN NEUTRON-IRRADIATED SOLID COMPOUNDS OF ARSENIC*

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Abstract—Some crystalline arsenic compounds have been irradiated with neutrons and the resulting chemical forms of radioactive arsenic separated by the method of paper electrophoresis. Heating the neutron-irradiated compounds of pentavalent arsenic (annealing) increased the percentage of activity separable as As(V). Analogous treatment of trivalent arsenic compounds decreased the already small percentage of pentavalent arsenic observed. Traces of radioactive elementary arsenic were also observed in the irradiated solids.

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THE phenomenon of thermal annealing, or recombination of recoil atoms in crystalline substances, is by now familiar, although by no means well understood.[1–6] This effect has been investigated in several oxyanion salts, for example potassium chromate[2] and bromate:[1] we thought that it would be of interest to extend these studies to the arsenic system, where not only oxyanion salts but pure oxides of arsenic could be investigated. In this way the annealing behaviour of the same recoil atom in a molecular and in an ionic crystal environment could be contrasted.

EXPERIMENTAL PROCEDURE

The materials used were of the purest reagent grade available. Precautions were taken to exclude moisture, as follows: sodium (meta) arsenite and (dibasic) arsenate were dried in an oven at 105° and 150° respectively. The sodium arsenite ($NaAsO_2$) showed no change in weight over a period of 24 hr heating while the sodium arsenate (Na_2HAsO_4), which was prepared from the heptahydrate, was dried to constant weight. The observed weight loss was 40·62 per cent (theoretical 40·42 per cent). Both samples were then stored *in vacuo* over silica gel. Arsenic trioxide (National Bureau of Standards) was dried at 105° for 24 hr; it showed no weight loss, and was also stored *in vacuo* over silica gel. The arsenic pentoxide was not heated but was stored *in vacuo* over silica gel for about three weeks before use.

All samples for irradiation were sealed *in vacuo* in quartz ampoules. In the case of the arsenic pentoxide the samples in their quartz tubes were heated while being pumped *in vacuo* at 100°C for several hours before sealing off.

All samples were maintained at dry-ice temperature (except when otherwise noted) during bombardment with neutrons in the Brookhaven reactor. The neutron flux was roughly 2×10^{12} neutrons cm^{-2} sec^{-1} and the duration of bombardment 3 min. Samples were then kept at dry-ice temperature until they were annealed or analysed.

* Research performed under the auspices of the U.S. Atomic Energy Commission.

† Guest Research Collaborator from the Chemistry Laboratory, Otaru College of Commerce, Otaru, Japan.

(1) J. COBBLE and G. E. BOYD, *J. Amer. Chem. Soc.* **74**, 1282 (1952).
(2) A. G. MADDOCK and M. M. DE MAINE, *Canad. J. Chem.* **34**, 275 (1956); M. M. DE MAINE, A. G. MADDOCK and K. TAUGBØL, *Faraday Soc. Disc.* **23**, 211 (1957).
(3) L. J. SHARMAN and K. J. MCCALLUM, *J. Amer. Chem. Soc.* **77**, 2989 (1955).
(4) A. H. W. ATEN, G. K. KOCH, G. A. WESSELINK and A. M. DE ROOS, *J. Amer. Chem. Soc.* **79**, 63 (1957).
(5) W. HERR, *Z. Elektrochem.* **56**, 911 (1952).
(6) H. RAUSCHER and G. HARBOTTLE, *J. Inorg. Nucl. Chem.* **4**, 155 (1957).

Annealing was carried out in constant-temperature (50 ± 0·5, 100 ± 0·5 and 200 ± 2°C) baths for specified periods of time, the samples remaining sealed in quartz. After annealing the quartz tubes were broken open and the samples were dissolved in 0·1 N sodium hydroxide solution containing arsenic (III) and (V) carriers. The quartz tubes were rinsed out with the same solution, and the rinsings were added to the main solution. Ten micro-litres of the resulting solution were then taken for the analysis into arsenate and arsenite by the method of paper electrophoresis.[6,7] Clean separations were obtained in about 2 hr; following this the paper was dried and cut into strips which were counted under thin-window, gas-flow proportional counters. Half-life determinations revealed that ^{76}As ($t_{1/2}$ = 26·8 hr) was the only significant radionuclide on the anion side of the electrophoresis strips. All experiments were carried out in (at least) duplicate. A typical electrophoresis histogram (radioactivity vs. distance along paper) is shown in Fig. 1, in which the broken histogram is the same as the solid, except that the vertical scale has been expanded 50-fold.

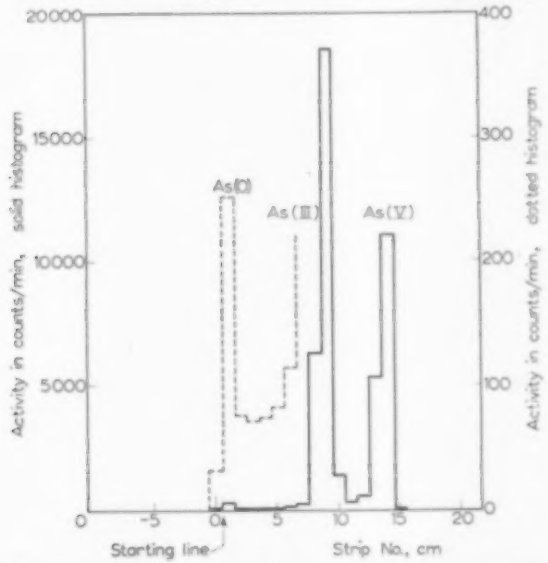

FIG. 1.—Histogram of electrophoresis pattern of irradiated arsenic pentoxide dissolved in 0·1 N NaOH containing As(III) and As(V) carriers. Electrophoresis paper wet with 0·01 N NaOH. Broken histogram refers to same data as solid line, but with 50-fold expansion of vertical scale.

RESULTS

All electrophoresis histograms of irradiated arsenic compounds showed the same system of three peaks as seen in Fig. 1, namely, a small peak close to the origin and two anion peaks. The latter were readily identified as arsenite and arsenate by chemical tests and by agreement of the observed activity ratios with previously published work.[8–10] The small peak at the origin may be tentatively identified as elementary arsenic, for the following reasons: (i) Its radioactive decay rate is the same as that of the other arsenic peaks. (ii) It is presumably uncharged since it does not move during electrophoresis. (iii) Arsenic produced in a Szilard–Chalmers reaction is only slowly attacked by dilute basic solutions.[11] This slow dissolution

[7] J. JACH, H. KAWAHARA and G. HARBOTTLE, Brookhaven National Laboratory Report BNL-3316 (1957).
[8] W. F. LIBBY, *J. Amer. Chem. Soc.* **62**, 1930 (1940).
[9] H. MÜLLER and E. BRODA, *Monatsh.* **82**, 48 (1951).
[10] P. SÜE, *J. Chim. Phys.* **45**, 177 (1948).
[11] A. G. MADDOCK and N. SUTIN, *Trans. Faraday Soc.* **51**, 184 (1955).

may be responsible for the appearance of activity between the arsenic and arsenite peaks, i.e. during the course of the electrophoresis some of the arsenic dissolves and "bleeds" out in the anion direction.

TABLE 1.—DISTRIBUTION OF ACTIVITY IN ARSENIC COMPOUNDS IRRADIATED WITH NEUTRONS

Compound	Temperature of irradiation	As(V) (%)	As(III) (%)†	As(O) (%)	Number of experiments included in average
As_2O_5	room	46·8 ± 1·7	51·9	1·32 ± 0·20	4
As_2O_5	dry-ice	40·8 ± 1·6	57·8	1·43 ± 0·30	4
As_2O_3	dry-ice	4·17 ± 0.30	94·8	1·06 ± 0·11	6
Na_2HAsO_4	dry-ice	55·9 ± 0·3	43·4	0·74 ± 0·06	2
$NaAsO_2$	dry-ice	4·6 ± 0·5	94·5	0·85 ± 0·2	2

† Percentage of As(III) quoted is by difference: (100 − average As(V) per cent − average As(O) per cent).

In Table 1 are given data from the analysis of irradiated arsenic compounds which were not annealed. In Figs. 2, 3, 4 and 5 are presented annealing data, i.e. the relation between the percentage of radioactive arsenic separable as arsenate and the time of isothermal heating.

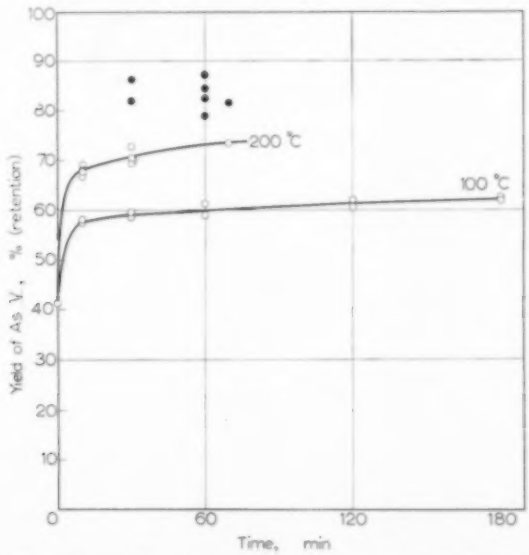

FIG. 2.—Thermal annealing in arsenic pentoxide. ●: samples which exhibited sintering on heating at 200°C. ○: samples which did not sinter. Each point represents one experiment.

In Fig. 2 it will be noted that there is considerable scatter in the 200°C annealing data and that points of two different kinds are given for that temperature. It was found after annealing at 200°C that some of the arsenic pentoxide samples had sintered into small globules, presumably because of traces of moisture which remained even after rigorous drying. The percentage of As(V) always seemed to be higher in

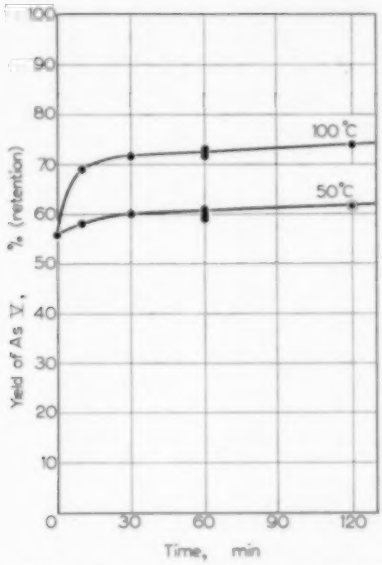

FIG. 3.—Thermal annealing in Na_2HAsO_4. Each point is the average of two experiments.

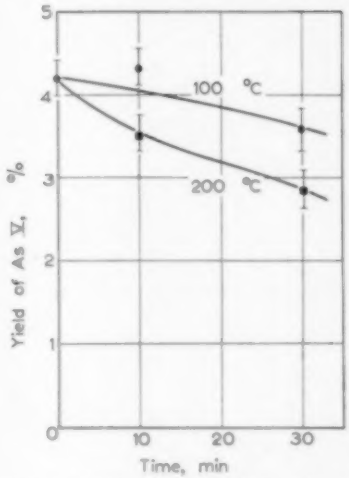

FIG. 4.—Thermal annealing in arsenious oxide. Each point is the average of two experiments.

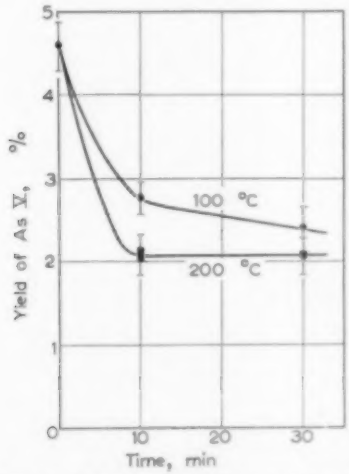

FIG. 5.—Thermal annealing in $NaAsO_2$. Each point is the average of two experiments.

these samples: for this reason samples which sintered and those which did not, at 200°C, are given different legends in Fig. 2. No sintering was observed in any of the other heated samples.

The analytical results for activity present as elementary arsenic were not so reproducible as those for As(V). Nevertheless, an interesting trend was evident in that in both the As(V) compounds the percentage of free arsenic tended to fall with annealing, while in the As(III) compounds it did not change, within experimental

error. Thus, annealing irradiated As_2O_5 for 30 min at 200°C reduced the arsenic (O) from roughly 1·4 per cent of the total activity to 0·7 per cent. A similar, although less marked decrease, was observed in Na_2HAsO_4.

DISCUSSION

Several other investigators have determined the distribution of radioactive arsenic in irradiated arsenious oxide. LIBBY[8] in early work found that 100 ± 2 per cent of the activity was present as As(III). MÜLLER and BRODA[9] give a curve for "AsIII-Kristall" from which one may estimate ~97% As(III). It is not clear whether their curve refers to As_2O_3 or $NaAsO_2$, both of which they irradiated. DE MAINE and MADDOCK[12] found As(V) ~1 per cent. Our value of ~4·2 per cent for the As(V) yield in As_2O_3 is thus somewhat larger than DE MAINE and MADDOCK's, and the difference may possibly arise from the lower temperature at which our neutron irradiation was conducted.

SÜE[10] reports 90% As(III) in irradiated $NaAsO_2$, while MÜLLER and BRODA[9] found 99 per cent for slow neutron and 90 per cent for epi-cadmium neutron irradiation. Our figure is 94·5 per cent for the mainly-thermal (cadmium ratio about 3) neutron flux in the Brookhaven reactor.

For Na_2HAsO_4 SÜE reported 60% As(V), MÜLLER and BRODA found ~70 per cent for dissolution in alkaline media: we find 56 per cent, and our lower figure is again presumably due to a lower ambient temperature of irradiation.

MÜLLER and BRODA indicate that in one experiment they warmed the Na_2HAsO_4 crystals to 95°C for 1 hr after irradiation. A similar experiment made by us (at 100°C) indicated (Fig. 3) that the retention (i.e. percentage As(V)) would thereby be increased from an initial value of 56 per cent to a final value of about 72 per cent. They found in their heated crystals As(V) ~ 67 per cent, in reasonable agreement with our own value but not greatly different from their (higher) initial value of 65 per cent for dissolution at pH 7. None of these investigators report the presence of elementary arsenic in any of their samples.

The annealing curves of As_2O_5 and Na_2HAsO_4 show the familiar shape characteristic of crystalline solids in general; namely, a rapid rise to a plateau whose value is dependent on the temperature. Several interpretations of this behaviour have been offered[2,13] but as yet it is difficult to find a wholly-satisfactory explanation. Of interest is the rarely-observed[5] behaviour exhibited by the As_2O_3 and $NaAsO_2$ crystals, namely, an annealing process in which there is a net reduction in oxidation state of the recoil atoms (Figs. 4 and 5). Clearly, the mechanism of oxide-ion or oxygen-atom recombination, which is invoked to explain annealing in cases where an increase in oxidation state takes place, cannot be applied. It may be that in this case some process such as

$$As^*O_3^- + As^+ \rightarrow As_2{}^*O_3 \qquad (1)$$

or

$$As_2{}^*O_5 + As_2O \rightarrow As_4{}^*O_6$$

occurs, where the species on the left, a radioactive As(V) and a hypothetical As(I) (inactive), are derived from a particular mode of breakup of the original As_2O_3

[12] M. M. DE MAINE and A. G. MADDOCK, *Canad J. Chem.* **34**, 441 (1956).
[13] F. P. CLARKE, *Faraday Soc. Disc.* **23**, 170 (1957).

(or As_4O_6) molecule. Annealing would thus have the net effect of transferring activity from the As(V) to the As(III) fraction. A similar process can be written for $NaAsO_2$.

A more likely possibility is the exchange of arsenic activity from the As(V) to the As(III) oxidation state through the equilibrium:

$$As_2O_3 + O_2 \rightleftharpoons As_2O_5. \tag{2}$$

Although air is excluded from the irradiated samples, oxygen molecules could still be produced in the displacement spike of the recoiling arsenic atom or by radiolysis of the crystals.

The behaviour of the As(O) fraction may be understood in terms of solid-state reactions. In the As(V) compounds, on heating, the As(O) atoms are simply oxidized

$$2As(O) + 3As(V) \rightarrow 5As(III) \tag{3}$$

although the mechanism undoubtedly involves only single arsenic (O) atoms oxidized in one- or two-electron steps. This process cannot take place, and is in fact not observed, in the two compounds of As(III).

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KINETICS OF THE REDUCTION OF INORGANIC IONS BY BOROHYDRIDE—I

FERRICYANIDE

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(*Received* 2 *September* 1958)

Abstract—The reaction of borohydride with ferricyanide to give borate and ferrocyanide has been studied in buffered aqueous solutions. The rate of disappearance of ferricyanide ion was found to be first order in both borohydride and hydrogen ion and independent of the ferricyanide ion with a normal bimolecular frequency factor of $5{\cdot}9 \times 10^{11}$ sec^{-1} and an activation energy of 7·2 kcal. A mechanism is proposed that is consistent with the kinetics of the hydrolysis of borohydride.

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THE reactions of borohydride in aqueous solution with various inorganic species have not been extensively investigated. The reactions with iodine, permanganate, hypochlorite have been studied from an analytical standpoint[1] and several other reactions have been surveyed by other workers.[2]

The only inorganic oxidant for borohydride which has been investigated kinetically is water.[3,4] The over-all stoicheiometry is:

$$BH_4^- + 2H_2O = 4H_2 + BO_2^- \qquad (1)$$

The hexacyanoferrate ions are an attractive choice for oxidation–reduction studies because in both oxidation states they are extremely stable with respect to dissociation and have the same geometry and chemical composition. Furthermore, only a one-electron transfer is involved. The over-all stoicheiometry involving the hexacyanoferrate ions is:

$$8\,Fe(CN)_6^{3-} + BH_4^- + 2H_2O = 8\,Fe(CN)_6^{4-} + BO_2^- + 8H^+ \qquad (2)$$

EXPERIMENTAL AND RESULTS

The kinetic studies were carried out by continuously following the concentration of ferricyanide from its absorption at 415 mμ with a Beckman spectrophotometer Model DK1 using 1 and 5 cm cells thermostated either with an air or water jacket. Sodium borohydride of 98 per cent purity was recrystallized[5] from diglyme* resulting in a product which gave by iodine titration[1] better than 99 per cent of theoretical reducing capacity. All other substances used were A.C.S. Analytical Reagent grade. Each run was performed both at constant borohydride and constant hydrogen ion concentrations. The borohydride concentration was kept essentially constant by using a large excess. Each run was buffered with either borate–boric acid, carbonate–bicarbonate or sodium hydroxide. The sodium hydroxide concentration was determined by titration with standard acid. The pH

* Diglyme has been suggested[5] as a name for the dimethyl ether of ethylene glycol.

[1] E. H. JENSEN, *A Study in Sodium Borohydride*. Nyt Fordisk Forlga, Copenhagen, (1954).
[2] For summaries see A. C. STEWART. Thesis, *Reducing Properties of Sodium Borohydride*, University of Chicago (1956); N. G. GAYLORD, *Reductions with Complex Metal Hydrides*. Interscience, New York (1956).
[3] R. L. PECSOK, *J. Amer. Chem. Soc.* **75**, 2862 (1953).
[4] J. B. BROWN and M. SVENSEN, *J. Amer. Chem. Soc.* **79**, 4241 (1957).
[5] H. C. BROWN, E. J. MEAD and B. C. RAO, *J. Amer. Chem. Soc.* **77**, 6029 (1955).

before and after a run was measured with a glass electrode and the hydrogen ion concentration was found to change by less than 10 per cent in any given run.

Three methods of mixing the reactants were used:

(1) adding solid sodium borohydride to a solution containing potassium ferricyanide;
(2) adding solid potassium ferricyanide to a solution containing sodium borohydride;
(3) mixing two solutions each containing one of the reactants.

As long as air was excluded no difference was found by the different mixing techniques.

The concentration ranges in moles per litre in these experiments were: initial ferricyanide from $1{\cdot}5 \times 10^{-4}$ to 18×10^{-4}, borohydride from 1×10^{-3} to 70×10^{-3} and hydrogen ion from 6×10^{-10} to 3×10^{-12}. In most of the runs the concentration of ferricyanide was followed until it dropped to less than a tenth of its original concentration.

The effect of continuous illumination of the reaction mixture in the spectrophotometer at 415 mμ was negligible. This was tested three ways: by using 1 and 5 cm cells, by working at different slit widths, and by keeping the reaction cell shutter closed 95 per cent of the time. Addition of ferrocyanide equal to the initial concentration of ferricyanide had no effect on the rate.

Two typical series of runs showing the variation in rate as a function of borohydride ion concentration at constant hydrogen ion are shown in Fig. 1. On Fig. 2 the log of the rate of disappearance of ferricyanide divided by borohydride ion concentration is plotted on the ordinate against pH on the abscissae. The nearly unit slope indicates a first order dependence on hydrogen ion. Fig. 3 shows that the second order over-all rate constants, k, obey an Arrhenius temperature relation with an activation energy of 7·2 kcal, and a frequency factor, A, of $5{\cdot}9 \times 10^{11}$ sec^{-1}.

The remainder of this section is a description of some nonkinetic experiments which are pertinent to a discussion of the mechanisms of the reaction. Bubbles of gas were observed to form in the reaction solution as the ferricyanide reacted. The bubbles were presumably hydrogen formed from the hydrolysis of borohydride as described by equation (1). Because the side reaction produces hydrogen, the possibility that ferricyanide catalysed the hydrolysis and the stoicheiometry over a wide range of concentration conditions were studied.

The possibility of catalysis of the hydrogen producing reaction by ferricyanide during conditions used in the kinetic studies was investigated. Aliquots of solutions in the concentration range used for the kinetic experiments, containing ferricyanide and an excess of borohydride, were analysed over the time range of the kinetic experiments. The JENSEN[5] iodimetric method for borohydride was modified to give the number of equivalents of borohydride present plus that portion of borohydride that had reacted with ferricyanide. This was done by adding zinc sulphate which insure the completion[6] of the reaction:

$$2Fe(CN)_6^{3-} + 2I^- \longrightarrow 2Fe(CN)_6^{4-} + I_2. \qquad (3)$$

Therefore, the iodine titre gives the difference between the number of equivalents of borohydride and ferricyanide. Since the titre remained constant within experiment error it was concluded that the ferricyanide does not catalyse the decomposition of borohydride.

The rate of hydrolysis of borohydride ion has been reported[4] as having the same dependence on the concentrations of hydrogen and borohydride ions which we have found for the rate of disappearance of ferricyanide. This led us to study the competition for borohydride ion by water and ferricyanide.

The information gained from these competition experiments will be used in conjunction with the kinetic results to propose a mechanism for the behaviour of the borohydride–ferricyanide aqueous system. Various ratios of ferricyanide to borohydride were prepared in 0·3 N NaOH. To these solutions, weak acids of different strengths were added at different rates while the reaction mixture was rapidly stirred. The hydrogen liberated from the hydrolysis reaction was determined volumetrically and the ferricyanide left was analysed spectrophotometrically. The conditions[6] of the experiment were such that all the borohydride either reacted with the water or the ferricyanide. Ten experiments were conducted with mole ratios of ferricyanide to borohydride of between 3 and 18 and initial ferricyanide concentrations from 0·03 to 0·4 M. In all cases the sum of the number of equivalents of hydrogen gas liberated and ferricyanide used up equalled within 3 per cent the initial amount of borohydride. The analyses showed that per mole of borohydride from 2·4 to 3·1 moles of ferricyanide were consumed with the corresponding liberation of 2·9–2·4 moles of H_2 gas. Most of the

[6] I. KOLTHOFF and E. SANDELL, *Textbook of Quantitative Analysis* p. 624. Macmillan, London (1946).

higher yields of ferricyanide reduction were found when the ratio of ferricyanide to borohydride was high and when the acid was added very slowly. For an interpretation of the kinetics we will consider it necessary that a proposed scheme should be consistent with the disappearance of 2–3 three moles of ferricyanide and the production of 2½–3 moles of hydrogen gas per mole of borohydride consumed.

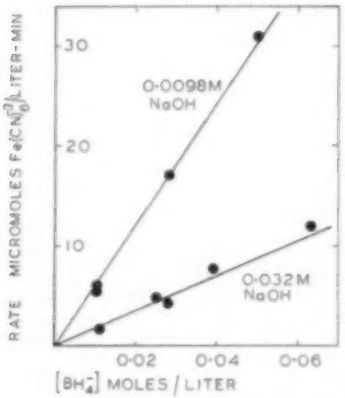

FIG. 1.—Rate of disappearance of ferricyanide vs. borohydride concentration. Upper curve at 0·0098 M NaOH, lower curve 0·032 M NaOH.

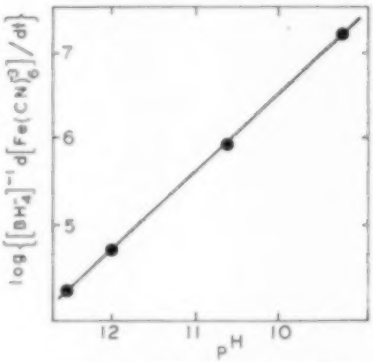

FIG. 2.—Hydrogen ion dependence: log of rate of disappearance of ferricyanide divided borohydride ion concentration vs. pH.

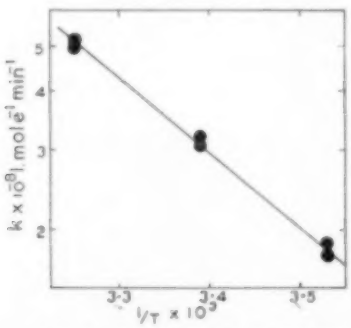

FIG. 3.—Arrhenius plot: second order rate constant, k, which is the rate of disappearance of ferricyanide divided by the concentrations of hydrogen ion and borohydride ion vs. reciprocal of absolute temperature.

DISCUSSION

The kinetics show that the activated complex for the rate determining step of both the hydrolysis (in the absence of ferricyanide) and the oxidation by ferricyanide is probably the same. Since the rates for both reactions are proportional to the first power of both the hydrogen and borohydride ions, it follows that the chemical composition of the activated complex is $H^+BH_4^-$. Further support for the identity of the activated complex comes from temperature studies. The over-all activation energy for the hydrolysis has been reported[3] to be within a kilocalorie of the value

obtained in our experiments with ferricyanide. The first step for both reactions is therefore:

$$BH_4^- + H^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H^+BH_4^-. \tag{4}$$

The redox steps following should involve 2 or 3 moles of ferricyanide per mole of borohydride consumed and produced $2\frac{1}{2}$–3 moles of H_2. From the present studies there is no evidence concerning the molecularities involved in these individual radox steps. There is evidence from the hydrolysis of diborane[7] that intermediates of partially hydrolysed boron hydride compounds exist and that these intermediates differ by two electrons in reducing capacity. They have one or more hydride hydrogens replaced by hydroxide groups. A mechanism consistent with these ideas would involve one- or two-electron steps.

Illustrated below are possibilities for one of the redox steps in the mechanism. Alternative one- and two-electron oxidations of the boron intermediate which has four equivalents of reducing capacity are given by equations (5–8). Equations (5) and (7) described a one-electron oxidation, by ferricyanide and water respectively, to produce the intermediate $BH(OH)_2^-$ which has three equivalents of reducing capacity. The two-electron reductions to produce $BH(OH)_2$, which has a two-electron reducing capacity, are described by equations (6) and (8).

$$BH_2OH + Fe(CN)_6^{3-} + H_2O \xrightarrow{k_{4F'}} BH(OH)_2^- + Fe(CN)_6^{4-} + 2H^+ \tag{5}$$

$$BH_2OH + 2Fe(CN)_6^{3-} + H_2O \xrightarrow{k_{4F''}} + BH(OH)_2 + 2Fe(CN)_6^{4-} + 2H^+ \tag{6}$$

$$BH_2OH + H_2O \xrightarrow{k_{4H}} BH(OH)_2^- + H + H^+ \tag{7}$$

$$BH_2(OH) + H_2O \xrightarrow{k_{4H'}} BH(OH)_2 + H_2 \tag{8}$$

The formulas of the boron intermediates used are primarily intended only to show the reducing capacity of the intermediate. The elemental hydrogen producing reactions probably involve a two-electron transfer. (Complex aluminium hydrides on hydrolysis in heavy water yield HD.[8])*

A kinetic scheme consisting of equation (4) followed by consecutive one-electron steps can be used as a basis to explain the experimental results. Each boron intermediate can react with either a ferricyanide or a hydrogen producing species such as water. Let the subscripts of the bimolecular rate constant, k, specify the reactants involved in the elementary step. The letter, i, which can be an integer from 1 to 8, refers to the reducing capacity of the boron intermediate, while "F" represents reaction with ferricyanide and "H" with a species producing hydrogen such as water. Assuming a steady state for each of the eight boron intermediates:

$$\frac{-d[Fe(CN)_6^{-3}]}{dt} = k_1[BH_4^-][H^+]\,\frac{k_{8F}[F] + k_{8H}[H_2O]}{k_{-1} + k_{8F}[F] + k_{8H}[H_2O]} \sum_{i=8,7,6,\ldots 1} \frac{k_{iF}[F]}{k_{iF}[F] + k_{iH}[H_2O]}. \tag{9}$$

* *Note added in proof:* Analysis of the hydrogen produced from the hydrolysis of our sample of $NaBH_4$ by heavy water was shown to contain over 90 per cent HD.

[7] H. G. Weiss and I. Shapiro, *J. Amer. Chem. Soc.* **75**, 1211 (1953); I. Shapiro and H. G. Weiss, *J. Phys. Chem.* **57**, 219 (1953).

[8] I. Wender, R. A. Friedel and M. Orchin, *J. Amer. Chem. Soc.* **71**, 1140 (1949).

Equation (9) consists of eight one-electron terms since each mole of borohydride has eight equivalents. Each term is obtained from the bimolecular rate constant, k_{iF}, times the product of the concentrations of the ferricyanide and the boron intermediate having an ith reducing capacity. The steady state concentration for the first intermediate, BH_5, is:

$$\frac{k_1[BH_4^-][H^+]}{k_{-1} + k_{8F}[F] + k_{8H}[H_2O]}. \tag{10}$$

The concentration for each succeeding steady intermediate with ith reducing capacity is equal to

$$[BH_5]\left\{\frac{k_{8F}[F] + k_{8H}[H_2O]}{k_{iF}[F] + k_{iH}[H_2O]}\right\}. \tag{11}$$

The general expression, equation (9), will agree with the experimentally observed kinetics (first order each in BH_4^- and H^+ and zero order in $Fe(CN)_6^{-3}$) and the observed ratio of reacted ferricyanide to produced hydrogen if three restrictions are imposed. First, two or three of the $k_{iF}[F]$ terms must be large compared to the corresponding $k_{iH}[H_2O]$. Second, the five or six remaining $k_{iF}[F]$ terms must be small compared to the corresponding $k_{iH}[H_2O]$ values. The first two restrictions make the summation factor in equation (9) equal to 2–3. Third, $k_{8F}[F] + k_{8H}[H_2O]$ must be large compared to k_{-1}. The k_{-1} is probably small since it was found that the experimental over-all rate constant has a normal collision frequency, 6×10^{11}. Using these restrictions, equation (9) becomes:

$$\frac{-d[Fe(CN)_6^{-3}]}{dt} = k_1[BH_4^-]\,[H^+] \times \text{(constant)} \tag{12}$$

with the constant having a value between two and three. Therefore, from the measurements on the ferricyanide kinetics, k_1, has a frequency factor of between 2 and 3×10^{11} sec^{-1} and an activation energy of 7·2 kcal. The essential feature is that any given intermediate reacts only with a hydrogen producing species, or else ferricyanide, i.e. that there be no competition for a given intermediate.

The same rate law will exist for a scheme with successive two-electron steps as long as any given ith boron intermediate is attacked either solely by a hydrogen producing species or the ferricyanide.

The proposed type of scheme also gives for the hydrogen gas produced which accompanies the reduction of ferricyanide:

$$\frac{d[H_2]}{dt} = k_1[BH_4^-]\,[H^+] \times \text{(constant)} \tag{13}$$

with this constant having a value between 2·5 and 3. The ratio of reacted $Fe(CN)_6^{-3}$ to produced H_2 should be independent of the initial ratio of ferricyanide to borohydride. This was confirmed experimentally, i.e. a wide variation in initial ratio resulted in a small change in the amount of ferricyanide reduced.

Further support for our mechanism is found from the rate measurements of the hydrolysis of borohydride in the absence of ferricyanide. The mechanism for the

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hydrolysis may be represented by equation (4) followed by hydrogen-yielding steps of the type given by equations (7) or (8). Then if k_{-1} is small compared to $k_{8H}[H_2O]$ the proposed mechanism predicts:

$$\frac{-d[BH_4^-]}{dt} = k_1[BH_4^-]\,[H^+] \tag{14}$$

We have measured the rate of hydrolysis of borohydride in borate buffers and found that our sodium borohydride had a rate constant, k_1, corresponding to a frequency factor 2×10^{11} sec^{-1}. This is in agreement with the value determined from the kinetic studies with ferricyanide.

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THE REACTION BETWEEN ALKALI MOLYBDATES AND MINERAL ACIDS*

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Abstract—In spite of extensive study, the precise nature of the reaction between alkali molybdates and mineral acids has been a controversial subject for several decades. A precise electrometric and spectrophotometric study has now shown that there is definite evidence for only one of the many proposed aggregation processes, namely that of molybdate to tetramolybdate. By following the effects of foreign electrolytes on the process, it has been found that activity and hydrolysis effects complicate the main reaction. The nature of "molybdate reagent" solutions is discussed with respect to these findings.

THE reaction between solutions of mineral acids and sodium molybdate solutions has been studied by pH and conductometric techniques by DUMANSKI *et al.*[2] by BRITTON and GERMAN,[3] by JANDER *et al.*[4] and more recently by BYÉ[5] and by CARPENI.[6] These workers have shown that molybdic acid does not behave as a dibasic acid with two widely differing acid dissociation constants. Thus, BRITTON and GERMAN,[3] using the quinhydrone electrode and a 0·045 M sodium molybdate solution found a pH titration curve which was initially buffered around pH 6 and in which one and only one inflexion was found, at the point corresponding with the addition of 1·5 equivalents of hydrochloric acid per sodium molybdate molecule. CARPENI,[6] using 0·2 M sodium molybdate and a glass electrode, found a similar curve, but one in which the inflexion fell at a position $1{\cdot}25 < [HCl]/[Na_2MoO_4] < 1{\cdot}35$. This inflexion was mildly time dependent: it also appears that the concentration of the solutions may have an effect on the position of the inflexion. BYE[5] who studied the pH values set up in the system (0·05 M Na_2MoO_4) in the presence of a large amount of neutral salt (2 M NaCl), again found a similar curve, but in this case the inflexion fell at $[HCl]/[Na_2MoO_4] = 1{\cdot}14$. Hence it appears that neutral salts also have an effect on the precise form of the titration curves.

The conductometric results found by various workers also differ in detail: the titration curves of DUMANSKI *et al.*,[2] JANDER *et al.*[4] and by BRITTON and GERMAN[4] all show a major change in direction when $[HCl]/[Na_2MoO_4] = 1{\cdot}5$, but the breaks observed by DUMANSKI *et al.*[2] are less sharp than those found by the others, owing to dilution effects, and JANDER *et al.*,[4] using 0·2 M sodium molybdate, found inflexions at $[HX]/[Na_2MoO_4] = 0{\cdot}65$ and 1·14. Again, DUMANSKI *et al.*[1] claimed to have found other breaks at $[HX]/[Na_2MoO_4] = 0{\cdot}5$ and 1·0, but when their results

* This study is part of work presented to the University of London for the degree of Doctor of Philosophy, April 1955.

† Present address: General Electric Research Laboratory, Schenectady, New York.

[2] DUMANSKI, BUNTIN, DIJATSCHOWSKI and KNIGA, *Koll. Z.* **38**, 208 (1926).
[3] BRITTON and GERMAN, *J. Chem. Soc.* 2154 (1930).
[4] JANDER, JAHR and HEUKESHOVEN, *Z. Anorg. Chem.* **194**, 406 (1930).
[5] BYÉ, *Bull. Soc. Chim.* **10**, 329 (1943).
[6] CARPENI, *C. R. Acad. Sci., Paris* **224**, 925 (1947).

are plotted, only a smooth curve is obtained, and even the break at $[HX]/[Na_2MoO_4] = 1{\cdot}5$ is not obvious until a dilution correction has been made. BRITTON and GERMAN[3] on the other hand found essentially no change in the conductivity of the system until $[HCl]/[Na_2MoO_4] \doteq 1{\cdot}5$, after which an increase was observed which was determined to be the same as that expected for the addition of free hydrochloric acid to the system. They therefore concluded that the reaction proceeded to the formation of a sodium polymolybdate, thus:

$$Na_2MoO_4 + xHCl \rightarrow (Na_2MoO_4)_{1-(x/2)}(MoO_3)_{x/2} + xNaCl + (x/2)H_2O$$

(where $x = 1{\cdot}5$, this would give sodium tetramolybdate) and that this sodium polymolybdate, behaving as the salt of an acid stronger than the hypothetical H_2MoO_4, resisted further attack by hydrochloric acid. JANDER *et al.*[4] however, claimed that sodium tetramolybdate underwent at least one more reaction to give an octamolybdate.

In order to rationalize the conflicting detail of the various reports, a careful study of the movements of the breaks and inflexions in the curves was made with respect to the composition of the solutions, all the time trying to establish the true composition of the solute molybdate. The neutralization of tetramolybdic acid (molybdic oxide dihydrate) was therefore studied along with the replacement of molybdic oxide from sodium (ortho) molybdate.

EXPERIMENTAL

Recrystallized sodium molybdate dihydrate (Found: MoO_3 59·44, 59·49; H_2O 15·06, 14·99. Calc. MoO_3, 59·53 H_2O 14·77%) which was free of phosphate and arsenate was used for the preparation of solutions. The molybdic oxide dihydrate was prepared by the method due to ROSENHEIM and BERTHEIM,[7] and stored in the dark. Supersaturated solutions were prepared from the bright yellow, ammonia-free crusts.

The glass electrode (Cambridge Instrument Co.) was calibrated frequently with the Universal Buffer of BRITTON and WELFORD[8] over the pH range 2·38–12·41, and below this with solutions of hydrochloric acid of known concentration. The normal calomel electrode was used as the reference electrode in all the pH studies. Conductometric titrations (at 1 kc/s) were performed using platinized platinum electrodes and a visual null point detector based on that described by HASZELDINE and WOOLF,[9] but having an additional sensitive amplifier applied to the signal leaving the bridge network. In this way very good sensitivities ($1/10^4$) were obtained, with full R–C nulling. Spectrophotometric studies were made using a Unicam SP 500 UV-visible spectrophotometer: samples of mixed sodium molybdate/hydrochloric acid solutions were run against the same thickness of sodium chloride solutions, whose concentrations were respectively equal to the initial concentrations of hydrochloric acid in each mixture.

DISCUSSION

The curves of the glass electrode titrations of sodium molybdate of various concentrations with hydrochloric acid solutions are shown on Fig. 1. They are similar in their general form; initially there is a small titre causing a sharp drop in pH, which is followed by a portion of the curve which is due to a strongly buffered solution in the vicinity of pH 6 to pH 5; subsequently, the addition of more than one equivalent of hydrochloric acid per sodium molybdate molecule brings the curves to the strongly marked inflexions in the region of pH 4, the more concentrated solutions (0·292 M, 0·146 M, 0·0365 M Na_2MoO_4) possessing this inflexion in the curves at positions corresponding with the addition of between 1·3 and 1·5 equivalents

[7] ROSENHEIM and BERTHEIM, *Z. Anorg. Chem.* **34**, 427 (1903).
[8] BRITTON and WELFORD, *J. Chem. Soc.* 1848 (1937).
[9] HASZELDINE and WOOLF, *Chem. & Ind.* 544 (1950).

of hydrochloric acid per sodium molybdate molecule, the inflexion occurring with the smallest amount of acid in the most concentrated solution. The most dilute solution of all (0·0023 M Na_2MoO_4) showed practically no change in direction at the position corresponding with the inflexions in the other curves. In the more concentrated solutions, the values of pH which were set up after the inflexion has been

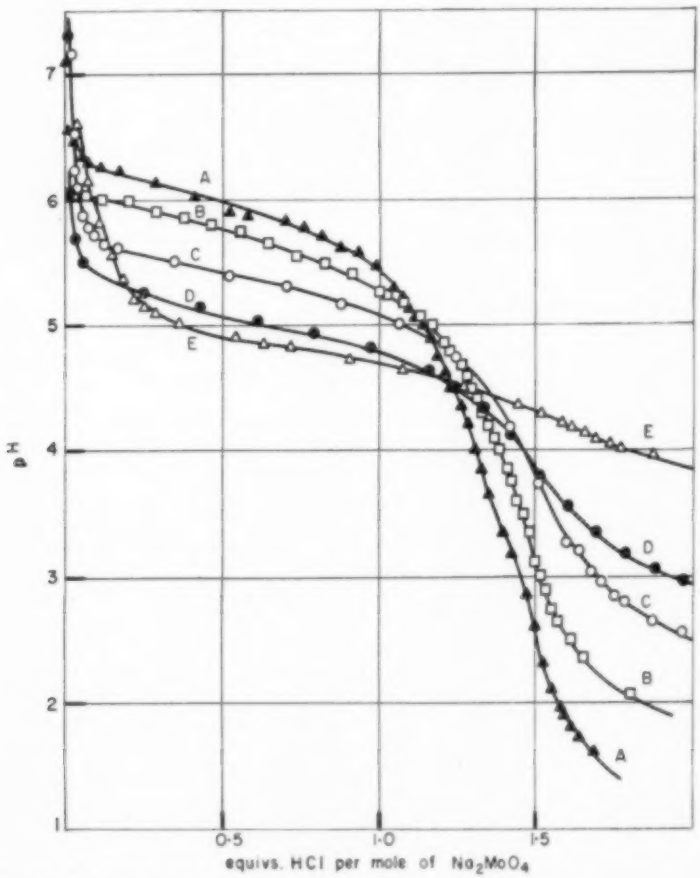

FIG. 1.—Glass electrode titrations of

A	50 ml	0·292 M	Na_2MoO_4	with	3·41 M HCl
B	50 ml	0·146 M	Na_2MoO_4	with	2·63 M HCl
C	50 ml	0·073 M	Na_2MoO_4	with	0·658 M HCl
D	50 ml	0·0092 M	Na_2MoO_4	with	0·164 M HCl
E	50 ml	0·0023 M	Na_2MoO_4	with	0·042 M HCl.

passed were very nearly those calculated for the addition of the same hydrochloric acid solution to a quantity of water of the same volume as the titrated solution at the endpoint.

The conductometric neutralization curves are also similar to one another (Figs. 2–5). Initially there was no appreciable change in conductivity, and until the amount of acid added exceeded one equivalent per sodium molybdate molecule, in no case was any change in direction of the curves observed. The overall effect in these initial

portions of the conductometric titration curves was a tendency for there to be a slight decrease in the value of specific conductivity, this decrease being relatively smaller with decreasing concentration of the solution under investigation. All the conductometric titration curves showed strongly defined breaks, at about 1·5 equivalents of acid per sodium molybdate molecule, the precise positions being tabulated below. In addition, a minor break was observed in the most concentrated solution (0·146 M Na_2MoO_4), on the addition of some 1·12 equivalents of hydrochloric acid per sodium molybdate molecule.

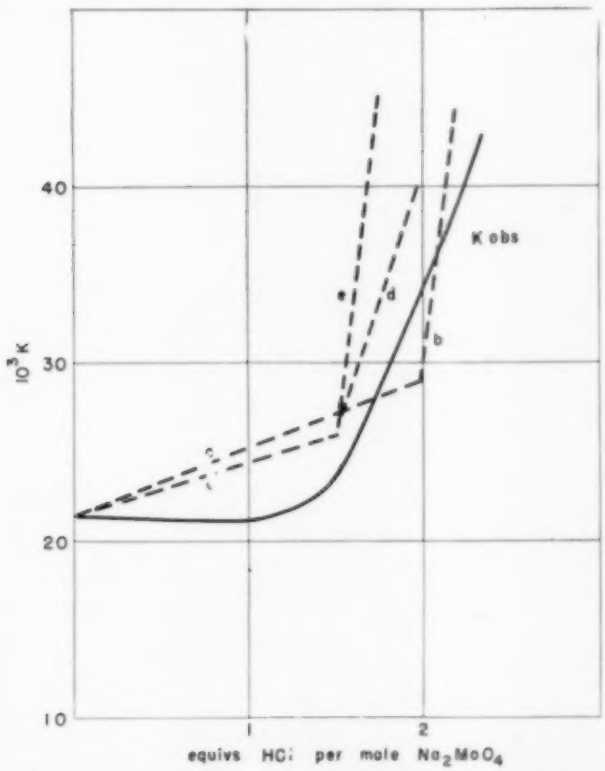

FIG. 2.—Conductometric titration at 25·0°C of 50 ml 0·146 M Na_2MoO_4 with 3·41 M HCl. Broken lines denote model reactions described in text.

The conductivity values were steady, but a little time was found necessary for the pH values to become steady, at the inflexion in the curve, in the most concentrated systems. A little more than 10 mins was required for this. The precise positions of the inflexions in the glass electrode titration curves are difficult to define, even when the differential method of plotting is used, since the inflexions are not nearly vertical. Consequently, from an analytical point of view, this method could only be of use if an accuracy of about 1 per cent were desired. The concentration to be employed for the molybdate solution should be of the order 0·08 M. The conductometric titration, on the other hand, provides an analytical method with an error of not more than 0·3 per cent, providing that the molybdate concentration lies between 0·07 M

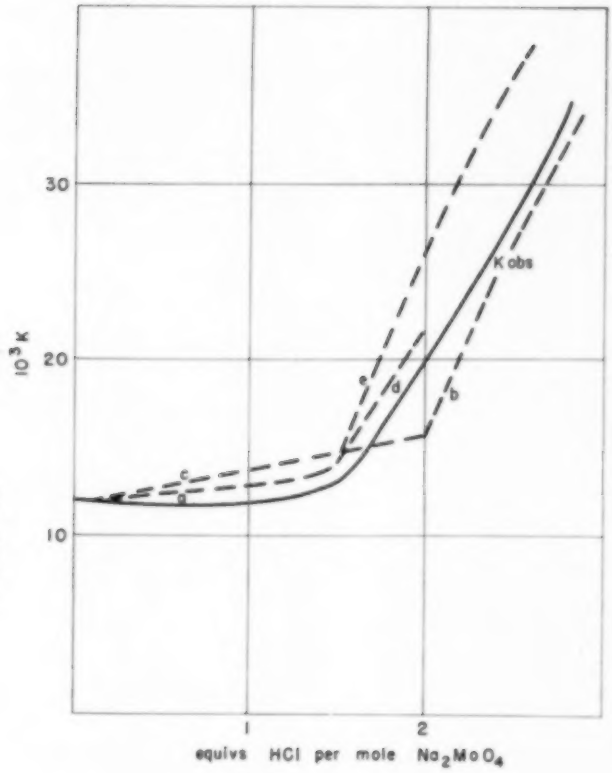

FIG. 3.—Conductometric titration at 25·0°C of 50 ml 0·073 M Na_2MoO_4 with 3·41 M HCl. Broken lines denote model reactions described in text.

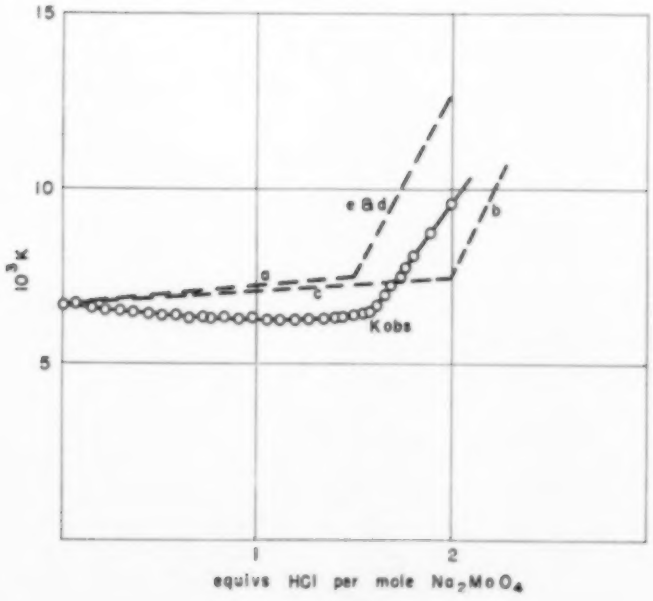

FIG. 4.—Conductometric titration at 25·0°C of 50 ml 0·0365 M Na_2MoO_4 with 0·658 M HCl. Broken lines denote model reactions described in text.

and 0·007 M, the break falling at exactly the position corresponding with the formation of sodium tetramolybdate, $Na_2O{\cdot}(MoO_3)_4$.

The position of the molybdate–tetramolybdate break has been observed to move slightly depending on the concentration of the solution with respect to molybdate.

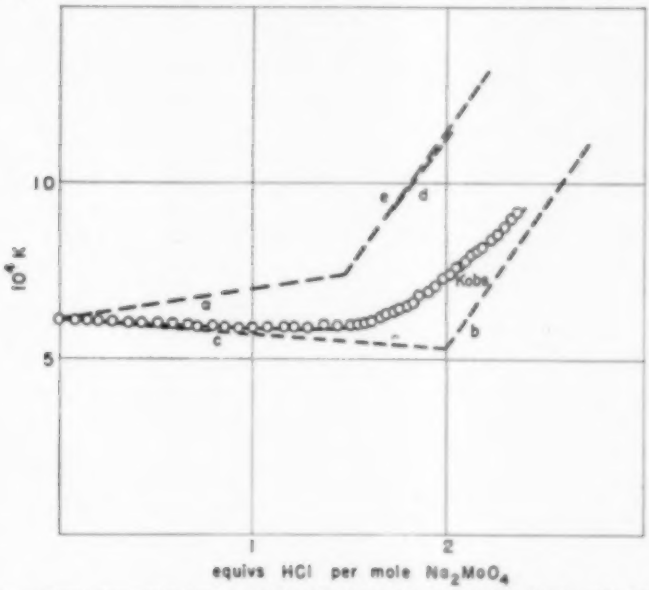

FIG. 5.—Conductometric titration at 25·0°C of 50 ml 0·0023 M Na_2MoO_4 with 0·041 M HCl. Broken lines denote model reactions described in text.

Thus, in very dilute solution (0·0023 M Na_2MoO_4) the break lies on the acid side of the titre required for the formation of sodium tetramolybdate, whereas in the more concentrated solutions it lies on the alkaline side (0·146 M Na_2MoO_4). The former observation was also made by BRITTON and GERMAN,[2] for in their titration of

TABLE 1.—THE POSITIONS OF THE BREAKS IN THE CONDUCTOMETRIC TITRATION CURVES OF SODIUM MOLYBDATE WITH HYDROCHLORIC ACID

Na_2MoO_4 (g mole/l.)	HCl (g mole/l.)	HCl : Na_2MoO_4 at break	Formulae of solute at break
0·146	3·41	1·48	$(Na_2O)_{0\cdot25}MoO_3$ $Na_2O.3.85MoO_3$
0·073	3·41	1·50	$(Na_2O)_{0\cdot25}MoO_3$ $Na_2O.4.0\ MoO_3$
0·0365	0·658	1·50	$(Na_2O)_{0\cdot25}MoO_3$ $Na_2O.4.0\ MoO_3$
0·0023	0·041	1·67	$(Na_2O)_{0\cdot16}MoO_3$ $Na_2O.6.25MoO_3$

0·005 M Na_2MoO_4 with 0·3289 M HCl, they obtained an endpoint which corresponded more nearly with the solute of composition $Na_2O{\cdot}5MoO_3$ than with that of composition $Na_2O{\cdot}4MoO_3$. It is quite possible that in dilute solution, the hydrolysis of the tetramolybdate ion is well advanced, according to the equation

$$O(MoO_3)_4^{--} + 3H_2O \rightarrow 4MoO_4^{--} + 6H^+$$

and hence the actual observed endpoint will be nearer that required for the reaction

$$Na_2MoO_4 + 2HCl \rightarrow H_2MoO_4 + 2NaCl$$

than to that required for the formation of sodium tetramolybdate. Further evidence for this idea may be gained from the glass electrode titration curves shown on Fig. 1. The titration of 0·0023 M sodium molybdate solution with 0·042 M hydrochloric acid solution gives a curve in which there was an indistinct inflexion between the positions corresponding with the addition of between one and two equivalents of hydrochloric acid per molybdate molecule. Also, were the final pH values in the titration governed only by the concentration of free hydrochloric acid present, assuming the reaction to form sodium tetramolybdate had occurred and was complete, then the expected hydrogen ion concentration would be approximately 0·0012 M at the position corresponding with the addition of two equivalents of acid per molybdate molecule. The pH corresponding with this concentration is less than 3, whereas the observed pH was higher (3·80). This suggests that the solution is buffered by some weakly acidic substance, for instance H_2MoO_4.

The actual conductivity values obtained during the titrations provide knowledge as to the course of the reaction with acid, at various concentrations of sodium molybdate. Thus, Figs. 2-5 show the observed values (thick lines) and certain calculated values, based on measurements made during this study. Thus, the line *c* shows the values to be expected were the system undergoing the reaction

$$Na_2MoO_4 + 2HCl \rightarrow H_2O + MoO_3 + 2NaCl,$$

it being assumed that the molybdic oxide formed made no contribution to the conductivity of the solution, and the line *b* corresponds with the addition of hydrochloric acid to a solution of sodium chloride of the volume and concentration that would be expected at the end of the above reaction, that is, at the position corresponding with the addition of two equivalents of hydrochloric acid per sodium molybdate molecule. The line *a* is that corresponding with the reaction

$$4Na_2MoO_4 + 6HCl \rightarrow Na_2O(MoO_3)_4 + 3H_2O + 6NaCl,$$

it being assumed that all the products, except the water molecules, are completely dissociated; the line *d* corresponds with the further reaction of sodium tetramolybdate with hydrochloric acid to form tetramolybdic acid, and the line *e* with the simple addition of free hydrochloric acid to a solution of sodium tetramolybdate, and sodium chloride of the volume and concentrations to be expected from the equation immediately above. It is seen that the observed values correspond most nearly with the two latter possibilities, that is, the formation of sodium tetramolybdate, with subsequent decomposition to tetramolybdic acid, and the addition of hydrochloric acid to sodium tetramolybdate. The titration was also carried well beyond the addition of two equivalents of hydrochloric acid per molybdenum atom, using more concentrated solutions of sodium molybdate (0·146 M) and hydrochloric acid (11·84 M). The values observed were less than those observed for the addition of hydrochloric acid solution to a solution of sodium chloride, of the same volume and concentration as would be expected on the basis of the above equation. This may suggest that the replacement of free tetramolybdic acid from its salts is an incomplete process even in the presence of a large excess of mineral acid, when the sodium molybdate

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concentration is relatively high. On the other hand, when the sodium molybdate concentration was low (0·0023 M), it was found that the observed values of conductivity fell nearer the values determined for the first reaction, namely

$$Na_2MoO_4 + 2HCl \rightarrow MoO_3 + H_2O + 2NaCl$$

The glass electrode titration curves of tetramolybdic acid with sodium hydroxide (Fig. 6) show inflexions after the addition of 0·5 and 2 equivalents of sodium hydroxide per molecule of molybdic oxide. Initially, the curves present a gradually rising portion, leading to the first inflexion, at which the pH lies between 3·5 and 4·5, after which the solution is well buffered until nearly two equivalents of sodium hydroxide solution have been added, when a very sharp change in direction is observed, and the pH values rise well into the alkaline region. The values were obtained readily, equilibrium being attained rapidly, until about 1·7 equivalents of alkali per molybdic oxide molecule had been added. Thereafter, about 2 hr were required for readings to become steady, particularly at the endpoint itself. After the endpoint had been passed, the values were once more steady within a period of seconds.

The conductometric titration curves show two breaks, at the positions corresponding with the inflexions in the glass electrode titration curves. Initially, the value of conductivity falls, as alkali is added to the solution of the acid, but after 0·5 equivalents of alkali per molybdic oxide molecule have been added, the values rise steadily until two equivalents of alkali have been added, when a still steeper rise commences.

The positions of the inflexions and breaks are thus very similar to those observed in the replacement titrations, and the neutralization of tetramolybdic acid may be represented thus:

$$H_2O(MoO_3)_4 + 2NaOH \rightarrow Na_2O(MoO_3)_4 + 2H_2O$$

$$Na_2O(MoO_3)_4 + 6NaOH \rightarrow 4Na_2MoO_4 + 3H_2O.$$

The substances mentioned, tetramolybdic acid and its sodium salt, have been previously investigated and the mode in which they exist is comparatively well understood (ROSENHEIM and BERTHEIM[7]). The observed values of conductivity during the neutralization of tetramolybdic acid have been compared with values calculated for the progress of the two reactions previously mentioned, and the values of the specific conductivity of tetramolybdic acid, sodium tetramolybdate and sodium molybdate at the concentrations of the titrated solution are shown on Fig. 7. The similarity of the observed and calculated values supports the idea of the two-stage neutralization, as also does the work of BRITTON and GERMAN,[3] who found constant values of pK for the hydrolytic reaction

$$O(MoO_3)_4^{--} + 3H_2O \rightarrow 4MoO_4^{--} + 6H^+$$

over the range 0·7–1·5 equivalents of alkali per molecule of molybdic oxide, thus confirming the hypothesis for the second stage.

The reaction of sodium molybdate with hydrochloric acid in the presence of neutral salts

Arising out of an observation by SOUCHAY and FAUCHERRE[10] concerning the titrations of solutions containing sodium molybdate and sodium phosphate in the

[10] SOUCHAY and FAUCHERRE. *Bull. Soc. Chim.* **18**, 355 (1951).

presence of sodium sulphate with hydrochloric acid, when an apparent alteration in the position of the inflexion occurred, it was decided to investigate the possibility that such neutral salts might affect the position of the inflexion when sodium molybdate

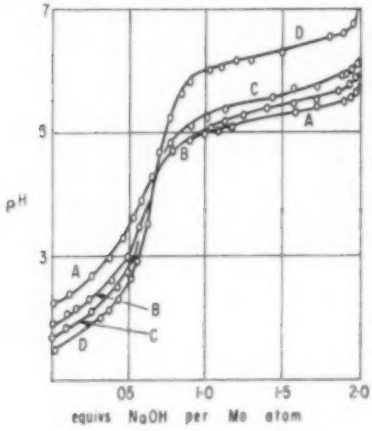

FIG. 6.—Glass electrode titrations of
A 50 ml 0·00979 M MoO_3 with 0·505 M NaOH
B 50 ml 0·0151 M MoO_3 with 0·505 M NaOH
C 50 ml 0·0310 M MoO_3 with 0·505 M NaOH
D 50 ml 0·0624 M MoO_3 with 1·01 M NaOH

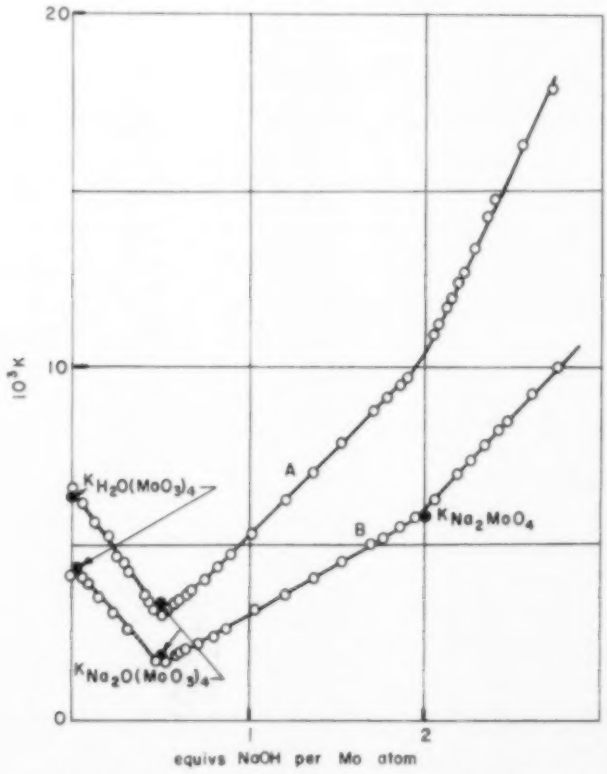

FIG. 7.—Conductometric titrations at 25·0°C of
A 50 ml 0·066 M MoO_3 with 1·144 M NaOH
B 50 ml 0·031 M MoO_3 with 0·505 M NaOH.

alone was titrated with hydrochloric acid, in the presence of other sodium salts. It has already been noted that BYE[5] found a change in the position of the inflexion when sodium molybdate was titrated with hydrochloric acid in the presence of sodium

chloride, and it was accordingly decided systematically to investigate the effect of sodium chloride and sodium sulphate upon the titration. The curves on Figs. 8–11 show the effect of the variation of sodium chloride concentration upon the titration curve of a fixed quantity of sodium molybdate (Figs. 8, 9) and the effect of varying the sodium molybdate concentration when the concentration of sodium chloride is held constant (Figs. 10, 11). It is seen that the presence of sodium chloride reduces the

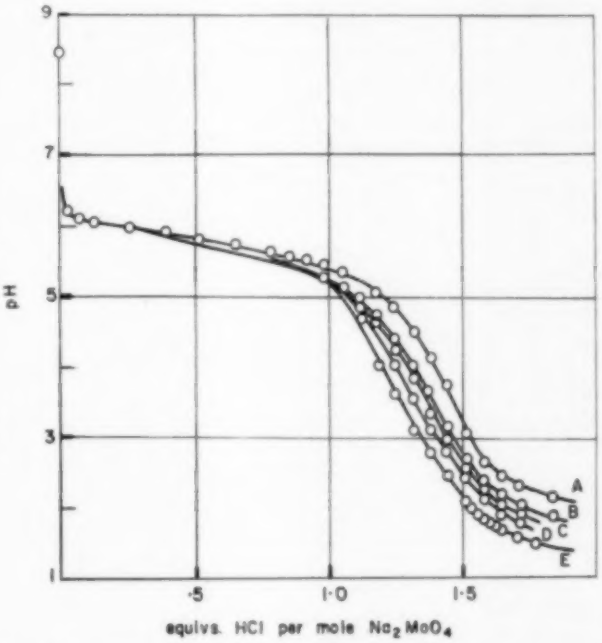

FIG. 8.—Glass electrode titrations of
A 50 ml of a solution 0·10 M Na_2MoO_4
B 50 ml of a solution 0·10 M Na_2MoO_4 and 0·38 M NaCl
C 50 ml of a solution 0·10 M Na_2MoO_4 and 0·75 M NaCl
D 50 ml of a solution 0·10 M Na_2MoO_4 and 1·5 M NaCl.
E glass and quinhydrone electrode titration of 50 ml of a solution 0·10 M Na_2MoO_4 and 3 M NaCl, all with 1·318 M HCl.

value of pH, for the addition of a given quantity of hydrochloric acid in excess of one equivalent per molecule of sodium molybdate, and further, a similar decrease in pH is observed on increasing the sodium molybdate concentration. It is probable that this latter effect is at least partly due to the first, by virtue of the sodium chloride formed in the reaction with hydrochloric acid. The effect of altering the molybdate concentration (Fig. 8) in the presence of sodium chloride is different from that observed in the absence of sodium chloride (Fig. 1). It is evident that less acid was required to lower the pH of the solution to a given value in the presence of sodium chloride than was required for sodium molybdate alone. This may be due to the formation of a less aggregated poly-ion in the presence of sodium chloride.

Titrations were also performed in the presence of sodium sulphate (Fig. 11). Here, the values of pH set up after the final inflexion had been passed were higher than those set up in aqueous solution and higher than those set up in sodium chloride solution of the same ionic strength. This led to the idea that the effect might be due to the nature of the added neutral salt, rather than to the ionic strength of the "solvent," since the high pH set up in the presence of sodium sulphate may be due to the comparative weakness of the second stage of dissociation of sulphuric acid, the free acid being made present by the interaction (in part at least) of sodium sulphate and hydrochloric acid. To test this idea, solutions of sodium chloride and sodium sulphate

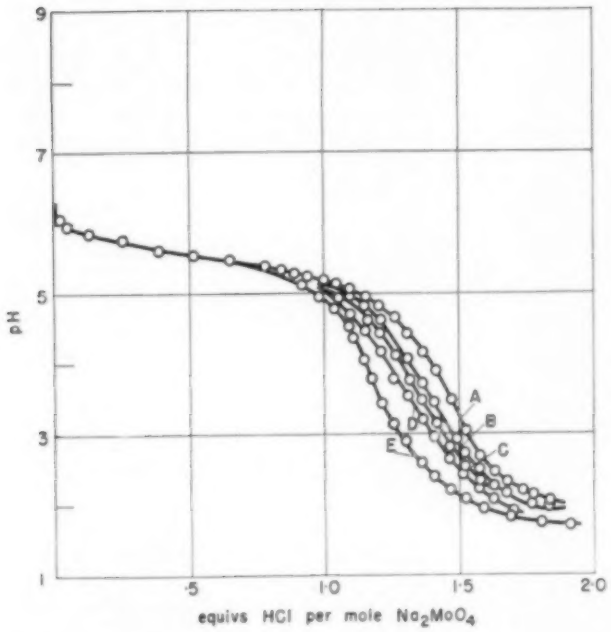

FIG. 9.—Glass electrode titrations of
A 50 ml of a solution 0·05 M Na_2MoO_4
B 50 ml of a solution 0·05 M Na_2MoO_4 and 0·38 M NaCl
C 50 ml of a solution 0·05 M Na_2MoO_4 and 0·75 M NaCl
D 50 ml of a solution 0·05 M Na_2MoO_4 and 1·5 M NaCl
E 50 ml of a solution 0·05 M Na_2MoO_4 and 3 M NaCl
all with 1·318 M HCl.

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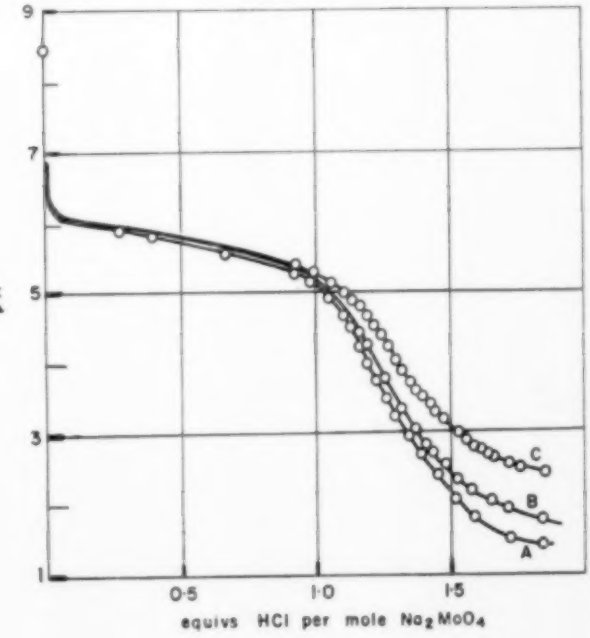

FIG. 10.—Glass electrode titrations of
A 50 ml of a solution 0·10 M Na_2MoO_4 and 3 M NaCl
B 50 ml of a solution 0·05 M Na_2MoO_4 and 3 M NaCl
C 50 ml of a solution 0·025 M Na_2MoO_4 and 3 M NaCl
with 1·318 M HCl (*A* and *B*) and 0·659 M HCl (*C*).

were titrated with hydrochloric acid solution, and the results compared with the values set up on adding hydrochloric acid solution to water. Here, the pH curve of the addition of hydrochloric acid to sodium sulphate lies above that for the addition of hydrochloric acid to water, which in turn lies above the curve for the addition of hydrochloric acid to sodium chloride solution. The decrease in pH in sodium chloride solution may be due to activity effects, since HARNED and OWEN[11] have

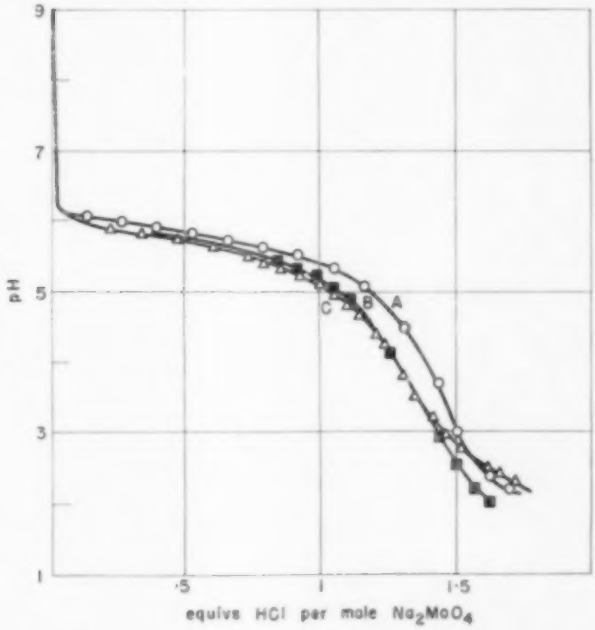

FIG. 11.—Glass electrode titrations of
A 50 ml of a solution 0·10 M Na_2MoO_4
B 50 ml of a solution 0·10 M Na_2MoO_4 and 0·75 M NaCl
C 50 ml of a solution 0·10 M Na_2MoO_4 and 0·301 M Na_2SO_4 with 1·318 M HCl.

shown that the mean ionic activity of hydrochloric acid first decreases in sodium chloride solution, but as the concentration of sodium chloride is increased, the activity of the acid increases very rapidly; thus 0·1 M HCl has a value of $\gamma\pm$ of 1·4 in 2 M sodium chloride, and the curve of $\gamma\pm$ HCl against the molality of sodium chloride rises very steeply after this.

The shift to the left in the inflexion may then do due to some salting out mechanism or to the formation of a different poly-ion, or to an activity effect. In connection with the formation of a different poly-ion, there was no visible precipitation or Tyndall cone effect when sodium chloride was used, but on one occasion with potassium chloride present, precipitation did occur, on the addition of strong mineral acid. The same behaviour, namely, the lessening of pH and the shift of the inflexion, was also observed when a solution of tetramolybdic acid in sodium chloride was titrated with alkali; but again there was no precipitation (Fig. 12). The effect of the change of neutral salt upon the titrations is best seen by reference to Fig. 11, which shows the titration curve of a solution of sodium molybdate in water, and in sodium chloride and sodium sulphate solutions of the same ionic strength. If an ion other than the tetra-ion is formed in these reactions, it is likely to be the so-called "para-ion,"

[11] HARNED and OWEN, *Physical Chemistry of Electrolytic Solutions* (2nd Ed.) p. 452. Reinhold, New York (1948).

$O(MoO_3)_{\overline{2\cdot8}}$, from the observed extreme position of the lower point of flex. It does seem quite likely that both para- and tetra-ions are formed in the aggregation process, since although this has not been conclusively demonstrated in the case of molybdates, there is a parallel behaviour with tungstates. However, there is no evidence for the formation of the para-ion at the lowest concentrations of molybdate studied. Since

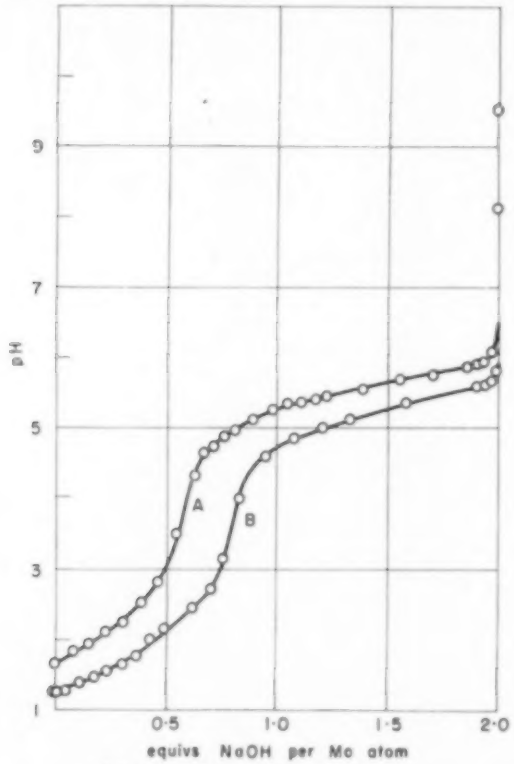

FIG. 12.—Glass electrode titrations of
A 50 ml of a solution 0·310 M MoO_3
B 50 ml of a solution 0·310 M MoO_3 and 3 M NaCl
with 0·505 M NaOH.

sodium chloride has a substantial effect in moving the inflexions to the left, which is explicable on the basis of an increase in the activity of the hydrogen ion, it seems entirely likely that the effects seen in the more concentrated molybdate systems are due to the sodium chloride liberated in the reaction. It is entirely possible to explain all the presently observed results on the basis of a simple one step ionic aggregation process, complicated by activity and hydrolysis effects, rather than a series of aggregations. Further support for the one stage idea may be gained from studies of ultraviolet absorption spectra.

The addition of hydrochloric acid causes the formation of aggregated polymolybdate ions, which sometimes have a faint yellow colour, in contrast to the colourless normal molybdate. This effect is shown very readily in the shift of the absorption curves towards the red end of the spectrum, on the addition of acid (Fig. 13, Table 2). All the curves appear to be portions of an absorption "edge"; that is to say, they

possess no peaks, and are consequently difficult to interpret. However, the close approximation of the curves *E*, *F*, *G* and *H* indicates that the polymerization ceases after the addition of about 1·5 equivalents of hydrochloric acid per sodium molybdate molecule, in agreement with the results of the preceding electrometric study.

TABLE 2.—CONCENTRATIONS OF SODIUM MOLYBDATE AND HYDROCHLORIC ACID IN THE SOLUTIONS WHOSE ABSORPTION SPECTRA ARE RECORDED ON FIG. 13

Solution	Na_2MoO_4 (g mole/l.)	HCl (g mole/l.)	$[HCl]/[Na_2MoO_4]$
A	0·07157	0·02584	0·361
B	0·07017	0·05066	0·722
C	0·06880	0·07451	1·083
D	0·06859	0·07819	1·140
E	0·06747	0·09716	1·440
F	0·06725	0·1009	1·500
G	0·06608	0·1196	1·81
H	0·06386	0·1386	2·17

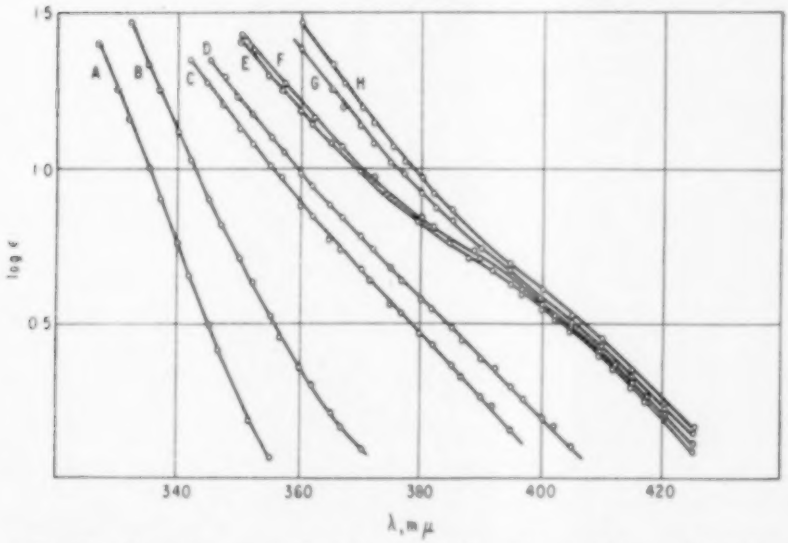

FIG. 13.—Absorption spectra of solutions containing sodium molybdate and hydrochloric acid, concentrations listed in Table 2.

The nature of "molybdate reagent" solutions

"Molybdate reagent" solutions are acidified solutions of ammonium molybdate, the free mineral acid concentration being quite high (approx. 2 N). The acidification is usually carried out in two stages, the first of which involves the addition of insufficient nitric acid to cause precipitation of molybdic oxide. This solution is then poured into the main bulk of the acid solution, thus apparently stabilizing the solution of "molybdic oxide" or tetramolybdic acid, which is highly supersaturated.

It was thought advisable to check whether the presence of ammonium ions had any effect on the aggregation process. Solutions of molybdate of a concentration comparable with that of the actual reagent could not be investigated, since the concentration was too high, and the corresponding values of conductivity too high to

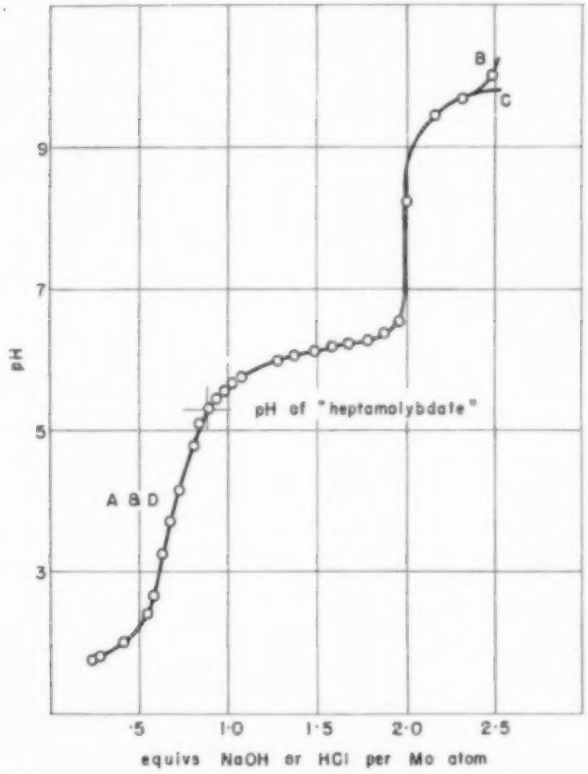

FIG. 14.–Glass electrode titrations of 50 ml of "ammonium paramolybdate" solution (MoO_3 = 0·202 M) with
A 3·68 M HCl
B 1·023 M NaOH
C 1·023 M NH_4OH and
D 50 ml 0·202 M Na_2MoO_4 with 3·68 M HCl.

be measured; likewise, the values of pH were too low. However, 50 ml portions of a solution 0·202 M with respect to molybdic oxide, prepared from ammonium hepta ("para") molybdate were titrated with 3·41 M hydrochloric acid, 1·023 M sodium hydroxide solution and 1·023 M ammonium hydroxide solution. The results are combined on Fig. 14, using different abscissae to permit the various curves to be shown on a common scale of equivalents of acid or alkali per molybdic oxide molecule. Also included on this figure is the glass electrode titration curve of 50 ml 0·202 M sodium molybdate with 3·41 M hydrochloric acid.

The various curves are seen to be superposable on one another, and consequently there is no difference in the aggregation process that can be detected by this method. It is therefore likely that molybdate reagent solutions contain tetramolybdic acid and ammonium tetramolybdate, in supersaturated solution, in the presence of ammonium nitrate and nitric acid.

Acknowledgements—I am grateful to the Senate and Council of the University of Exeter, the Ministry of Education of H.M. Government and the Foundation Governors of King Edward VI School, Totnes for scholarships and grants, and to Imperial Chemical Industries Ltd. for a gift of apparatus.

J. Inorg. Nucl. Chem., 1959, Vol. 9, pp. 267 to 272. Pergamon Press Ltd. Printed in Northern Ireland

MOLYBDIC ACID AND ITS ORGANIC COMPLEXES—I

SOME STUDIES ON MOLYBDIC ACID PREPARED BY ION EXCHANGE

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(*Received* 30 *June* 1958)

Abstract—An ion exchange method is described for the preparation of molybdic acid in more concentrated solution than that obtained by dissolution of yellow molybdic acid, $MoO_3 2H_2O$. This acid has been examined potentiometrically and conductometrically by titration with sodium hydroxide and the resultant titration curves have been found to depend on the concentration of the molybdic acid solution used. Evaporation to dryness of the molybdic acid solution prepared by ion exchange yields a colourless glass. Commercial molybdic acid has also been examined.

SEVERAL types of molybdate ion have been suggested to exist in molybdate solutions at various pH values. These include MoO_4^{2-}, $Mo_3O_{11}^{4-}$, $Mo_6O_{21}^{6-}$, $Mo_{12}O_{41}^{10-}$ which have been claimed by JANDER[1] and by BRINTZINGER,[2] $Mo_7O_{24}^{6-}$ and $Mo_4O_{13}^{2-}$ by BYÉ,[3,4] and $Mo_8O_{26}^{4-}$ by LINDQVIST.[5] Experimental justification for these suggestions has been based on diffusion and dialysis studies on partially neutralized alkali molybdate solutions and by potentiometric and conductometric titrations on similar solutions with mineral acid. Various results have been obtained by different workers using the latter method; for example JANDER[1] claims a break corresponding to $5R_2O{\cdot}12MoO_3$, whereas BYÉ[4] claims that the break occurs at the acidity corresponding to $3R_2O{\cdot}7MoO_3$. Much of the confusion which exists is due to the lack of data on the reverse procedure, that is, the progressive neutralization of molybdic acid with alkali. These data are difficult to obtain since, molybdic oxide, MoO_3, is almost insoluble in water and molybdic acid dihydrate prepared by Auger's[6] method, the only well established molybdic acid, will only form an 0·05 M solution (w.r.t. MoO_3) at room temperature. BYÉ[4] has found only one break in the conductivity curve obtained by titrating this acid near its limiting solubility with sodium hydroxide. This corresponds to the formula R_2O4MoO_3 but BYÉ[4] suggests this single intermediate break is due to the low concentration of the molybdic acid used. In the present study an attempt has been made to prepare a molybdic acid solution by ion exchange comparable in concentration with the molybdate solutions used by JANDER,[1] and to determine the Na : Mo ratio at the breaks in the curves obtained on potentiometric and conductometric titration of this acid with sodium hydroxide.

An investigation has also been made of commercial molybdic acid described as "suitable for analysis" which is manufactured by addition of nitric acid to ammonium molybdate, then heating to decompose the ammonium hydrogen molybdates.

[1] G. JANDER, K. F. JAHR and W. HEUKESHOVEN, *Z. Anorg. Chem.* **194**, 383 (1930).
[2] H. BRINTZINGER and W. BRINTZINGER, *Z. Anorg. Chem.* **196**, 55 (1931).
[3] J. BYÉ, *Ann. Chim.* **20**, 463 (1945).
[4] J. BYÉ, Thesis, Paris (1945).
[5] I. LINDQVIST, *Nova Acta Reg. Soc. Sci. Upsala* **15**, 1 (1950).
[6] V. AUGER, *C.R. Acad. Sci., Paris* **206**, 913 (1938).

EXPERIMENTAL

A solution was made by dissolving 12·1 g of sodium molybdate in 200 ml of distilled water and it was passed slowly through a prepared column containing sufficient Zeo-Karb 225 (a sulphonated polystyrene cation exchange resin) in the hydrogen form, to ensure complete exchange. The liquid collected was clear to the naked eye and without any trace of "molybdenum blue". To ensure complete removal of the sodium, the column was regenerated and washed until the liquid emerging had a conductivity of 3 μmhos or less; then the molybdic acid was recycled through the column. To obtain a solution of maximum concentration, the first two bed volumes of molybdic acid were rejected. For most purposes, however, the whole of the material was collected and diluted to 500 ml. This yielded with reasonable reproducibility a 0·085 molar solution (w.r.t. MoO_3) of molybdic acid. This solution is strongly acidic (pH = 2·1) and has a high conductivity ($0{\cdot}511 \times 10^{-2}$ mhos at 20°C). Attempts were made to prepare an 0·5 molar solution but some reduction occurred within the column. The acid in 0·085 M solution is stable in a stoppered bottle but is partially reduced to "molybdenum blue" by most reducing agents.

The concentration of molybdic acid was determined gravimetrically by precipitation with 8-hydroxy-quinoline. All pH measurements were made using a Cambridge pH meter with a glass-calomel electrode system calibrated with buffer solutions complying with accepted standards. All conductivity measurements were made with a Mullard Conductivity Bridge. All experiments were conducted at 18°C unless otherwise stated.

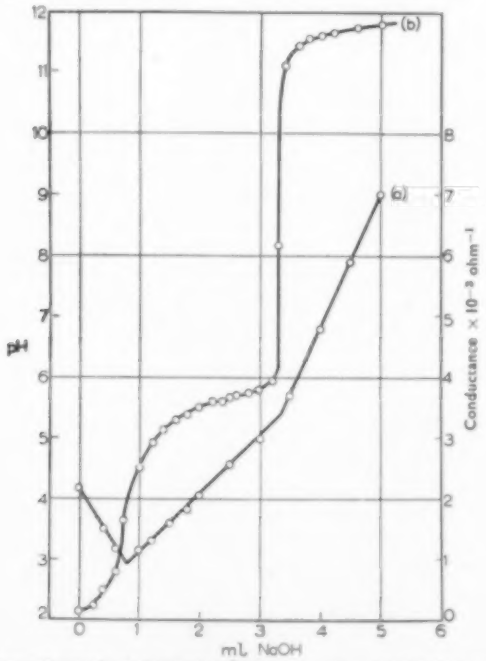

FIG. 1.—Potentiometric and Conductometric titration of 0·034 M molybdic acid.
(a) Conductometric titration.
(b) Potentiometric titration.

RESULTS AND DISCUSSION

Figs. 1–3 represent the curves obtained by potentiometric and conductometric titration of the molybdic acid at three concentrations with sodium hydroxide. The curves shown in Fig. 1 were obtained by titration of 50 ml of approximately 0·034 M molybdic acid (as MoO_3) with N·NaOH. This solution is comparable in concentration with that used by BYÉ[4] who used yellow molybdic acid ($MoO_3 2H_2O$) prepared

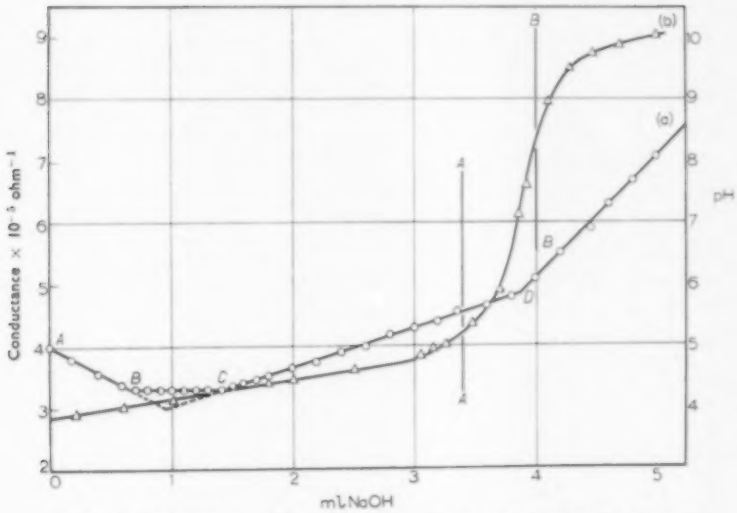

FIG. 2.—Potentiometric and Conductometric titration 0·00034 M molybdic acid.
(a) Conductometric titration.
(b) Potentiometric titration.

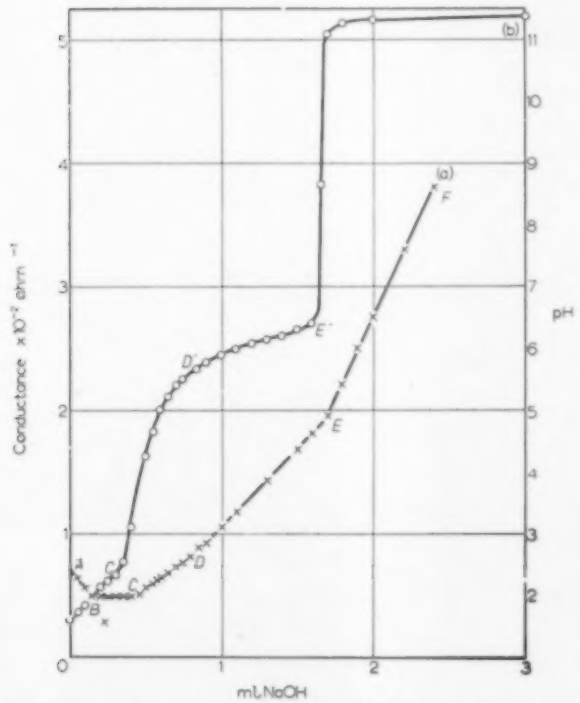

FIG. 3.—Potentiometric and Conductometric titration 0·22 M molybdic acid.
(a) Conductometric titration.
(b) Potentiometric titration.

by AUGER's[6] method. The curve obtained by conductometric titration Fig. 1(a) is similar to that described by BYÉ[4] and has breaks corresponding to ratios of 1Na : 2Mo and 4Na : 2Mo. Similar results were obtained by titrating 0·02 M molybdic acid. The first break in the conductivity curve occurs at the same Na : Mo ratio as the point of inflexion in the pH titration and corresponds to the neutralization of the readily replaceable hydrogen of a strong acid. This break at the ratio 1Na : 2Mo is in accordance with many of the formulae proposed for the state of aggregation of molybdic acid in fairly concentrated solution. These include $H_2Mo_2O_7$ suggested by FREY[7] with one strongly acidic hydrogen. ($NaOH + H_2Mo_2O_7 \rightarrow NaHMo_2O_7 + H_2O$) $H_2Mo_4O_{13}$ as suggested by CARPÉNI,[8] $H_6Mo_6O_{21}$, with three easily replaceable hydrogen ions suggested by JANDER[1] or $H_4Mo_8O_{26}$ as suggested by LINDQVIST.[5] The latter ion is supposed by LINDQVIST to be stable within the pH range 1·5–2·9 and to be formed reversibly from $Mo_7O_{24}^{6-}$ in all fairly concentrated solutions at these pH values. The initial pH of the solution used (2·4) is well within this range but that corresponding to neutralization, 3·75, lies outside the range of values: according to LINDQVIST[5] at this pH only $Mo_7O_{24}^{6-}$ should be present. No break corresponding to this latter Na : Mo ratio was found in either the conductance or the pH titration at this particular concentration.

The exact state of aggregation of the ion cannot be deduced from either potentiometric or conductometric titration, so further discussion without additional evidence is merely speculation. It is of interest to observe, however, that cryoscopic measurements by CARPÉNI[8] have indicated a fourfold aggregation in dilute acidified molybdate solutions giving an ion $Mo_4O_{13}^{2-}$. DOUCET and BUGNON[9] have also shown, using conductivity and freezing point methods, that in a solution of yellow molybdic acid, $H_2Mo_4O_{13}$ is the lowest polymer present.

The second break in the conductivity curve occurs at the same Na : Mo ratio as the point of inflexion in the pH titration curve and corresponds to the complete formation of Na_2MoO_4. The concentration of molybdenum as Na_2MoO_4 determined in this manner agrees exactly with that determined gravimetrically by precipitation as the oxinate. Both the conductivity and pH values became steady almost immediately after each addition of sodium hydroxide throughout the whole of the titration. Thus equilibrium between the aggregated ion and the MoO_4^{2-} ion (if this is accepted as existing in stoicheiometric Na_2MoO_4) is established rapidly on addition of sodium hydroxide. This is in marked contrast to the results obtained by titration of a similar quantity (50 ml) of dilute molybdic acid (0·00034 M) with 0·01 N NaOH (Fig. 2). In the latter part of this titration equilibrium was attained extremely slowly. The results of the conductometric titration Fig. (2a) correspond initially, *AB*, to the neutralization of the hydrogen of a strong acid; a flat portion, *BC*, which is reproducible is obtained immediately afterwards. Equilibrium is established quickly during this stage in the titration and *BC* on the basis of the conductivity studies above could be explained as due to hydrolysis of the salt formed in the very dilute solution. On extrapolation *AB* and *CD* intersect at an Na : Mo ratio of 1 : 2 similar to that obtained above (Fig. 1). It is of interest to note that no point of inflexion is obtained at this Na : Mo ratio during the potentiometric titration of the acid (Fig. 2b). The

[7] H. FREY, *Ann. Chim.* **18,** 1 (1943).
[8] G. CARPÉNI, *Bull. Soc. Chim. Fr.* **14,** 484 (1947).
[9] Y. DOUCET and S. BUGNON, *J. Chim. Phys.* **54,** 155 (1957).

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pH of the dilute solution is 3·84 at the commencement of the titration whereas the pH at the point of inflexion during the neutralization of the more concentrated acid used previously (Fig. 1) is 3·75. It is possible, therefore, that the titration in Fig. 2 represents essentially only the second portion of that recorded in Fig. 1. The effect of increasing the ionic strength of the solution was investigated by repeating the titration in a solution 0·1 N with respect to KCl. Addition of the potassium chloride merely depressed the measured pH slightly throughout the titration.

The most concentrated molybdic acid investigated, 0·22 M was comparable in strength to the alkali molybdate solutions used by JANDER.[1] The results of a conductometric and potentiometric titration of 20 ml of this solution with 5 N NaOH are recorded in Fig. 3. *AB* corresponds again to the progressive neutralization of the hydrogen ion of a strong acid but at this concentration it appears that decomposition of the acid commences at *B* before the acid has been completely neutralized. By titrating the acid quickly the conductivity falls from *B* along the dotted line *BX* (Fig. 3) but if the solution is allowed to stand after addition of each aliquot of sodium hydroxide the line *BC* is obtained. Similar results are obtained on potentiometric titration of the acid. These non-equilibrium values obviously correspond to the neutralization of further hydrogen ions from the acid originally present which is unstable after pH 2·0 and slowly reverts to another form in solution. Decomposition of the acid continues with a small increase in conductivity to the point *C* which corresponds to an Na : Mo ratio of 1 : 2. From *C* the conductivity increases, then a further break occurs at *D* after which the conductivity rises more rapidly to *E* which corresponds to the complete formation of Na_2MoO_4. Since the lines *CD* and *DE* do not differ appreciably in slope, the point of intersection *D* is not sharp. This point, however, corresponds approximately to the Na : Mo ratio found in the paramolybdates on the basis of the formula $R_6Mo_7O_{24}$.

The number of replaceable hydrogen atoms in the acid originally present in this solution is difficult to determine since it decomposes before complete neutralization. From the shape of the graph, however, it would appear that the Na : Mo ratio is less than 1 : 2 and thus the ion formed in solution is probably from some poly acid of the form $H_2Mo_9O_{28}$. Further evidence for the existence of a more aggregated acid in the concentrated solution is obtained from a study of the time required for equilibrium after dilution of the solution with distilled water. A 1 : 10 dilution of the concentrated acid produced a solution comparable in strength with that examined in Fig. 1. The conductivity of this solution varied from $0{\cdot}130 \times 10^4$ μmhos immediately after dilution to a constant value of $0{\cdot}170 \times 10^4$ μmhos which was obtained after an interval of 5 min. Further dilution of the latter solution (to 1 : 10,000) produced no further time variable change.

Thus if the results of these three figures are considered, it appears that at low concentrations only one intermediate break in the conductivity curve is observed corresponding to an aggregated acid of the form $H_2Mo_4O_{13}$ as noted previously by other workers. At higher concentrations, however, further breaks are observed at points corresponding probably to the formation of the paramolybdate ion and also initially to the existence of an ion of higher molecular weight. No evidence has been found, however, for the existence of the other aggregated ions reported by JANDER.[1]

Although the acid in dilute solution gave the same titration curve with sodium hydroxide as that produced by a solution of AUGER's[6] molybdic acid $MoO_3 2H_2O$,

evaporation to dryness of the former acid did not yield AUGER's acid. Samples of the ion exchange acid which were allowed to evaporate under various conditions yielded in every case a colourless glass which exhibited conchoidal fractures. LINDQVIST[5] has described a similar glass which was formed during the spontaneous evaporation of a sample of mother liquor from one preparation of $MoO_3 2H_2O$ which was allowed to stand undisturbed for six months.

For the sake of comparison, some commercial molybdic acid was also examined. This acid was described as "suitable for analysis" and was prepared* by acidification of ammonium molybdate, then heating to decompose the ammonium hydrogen molybdates. This material was found to be only very sparingly soluble in cold water but dissolved in boiling water to form a solution containing 0·35 per cent by weight of MoO_3. The molybdenum in the dry material was determined gravimetrically by precipitation as the oxinate and the ammonia by a Kjeldahl distillation. The results showed that the material contained 5·43 per cent of ammonia and molybdenum corresponding to 89·15 per cent of MoO_3. The material presumably hydrates on dissolution in hot water, the conductivity increasing linearly on addition of NaOH until the ratio 3Na : 2Mo is almost obtained. After this point a straight line parallel to the axis is obtained, corresponding to the displacement of ammonia from the complex. This material has been found suitable for the investigation of complex formation between organic polyhydroxy compounds and molybdate ions in the presence of ammonia and the results of these experiments will be reported in a later paper.

Acknowledgement—The author wishes to thank MR. H. BUCHWALD for the gravimetric determination of molybdenum.

* Data supplied by manufacturers.

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MOLYBDIC ACID AND ITS ORGANIC COMPLEXES—II

COMPLEX FORMATION BETWEEN MOLYBDIC ACID AND POLYHYDROXY ORGANIC COMPOUNDS

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(*Received* 14 *July* 1958)

Abstract—Complex formation between molybdic acid and a wide range of polyhydroxy compounds has been investigated. Complex formation between molybdic acid and erythritol, gluconic acid galactonic acid and arabonic acid has been found to occur. Glycerol penta-erythritol and all of the sugars examined show little tendency to complex. The effect of progressive addition of sodium hydroxide to the erythritol complex has been studied conductometrically.

COMPLEX formation between molybdic acid and organic compounds containing hydroxyl groups has been reported by several authors.[1,2] RIMBACH and LEY[1] studied the effect of glycollic, lactic, malic, citric and tartaric acids, glycol, glycerol mannitol and dextrose on molybdic acid and ascribed the resulting increase in acidity, to complex formation between hydroxyl groups. Complex formation between mannitol and molybdic acid has been studied by GERNEZ,[3] TANRET,[4] HONNELAITRE[5] and by FREY,[6] who has described a method for the preparation of the solid complex. Much of the information available on the other complexes is qualitative only and the molybdic acid used was often of doubtful purity. It was decided, therefore, to extend these investigations using molybdic acid from various sources employing conductometric and potentiometric techniques.

EXPERIMENTAL

It was considered desirable in this study to use molybdic acid of high purity. Unfortunately, molybdenum trioxide, which can be obtained extremely pure, is insoluble in water, and although various polyhydroxy alcohols increase the conductivity and decrease the pH of the aqueous solution the solubility of the trioxide is not appreciably increased. Commercial molybdic acid described as "suitable for analysis" was also examined and found to be suitable for many studies; although it is insoluble in cold water it is more soluble in hot and is quite soluble in a cold solution of many polyhydroxy compounds. Commercial molybdic acid contains appreciable quantities of ammonia although otherwise it is quite pure. The presence of the ammonia is useful, however, in many investigations since FREY has described a complex between mannitol and molybdic acid in which she claims ammonia is an integral part. Commercial molybdic acid was used by FREY[6] in this preparation.

Pure molybdic acid was prepared by passing a solution of sodium molybdate through a column

[1] E. RIMBACH and P. LEY, *Z. Physik. Chem.* **100**, 393 (1922).
[2] A. B. BISWAS, *J. Indian Chem. Soc.* **24**, 345 (1947).
[3] D. GERNEZ, *C.R. Acad. Sci., Paris* **112**, 1360 (1891).
[4] G. TANRET, *Bull. Soc. Chim. Fr.* **29**, 670 (1921).
[5] A. HONNELAITRE, *Ann. Chim.* **3**, 5 (1925).
[6] H. FREY, *Ann. Chim.* **18**, 1 (1943).

containing a cation exchange resin (Zeo Karb 225), in the hydrogen form. The properties of this acid have been described in a previous paper in this series.

All pH measurements were made using a Cambridge pH meter and a glass–calomel electrode system. All conductance measurements were made using a Mullard Conductivity Bridge operating in the most sensitive range and a cell of constant 1·459.

Lusteroid plastic test tubes were used in most of the experiments in preference to glass tubes. This avoided any possible contamination of the molybdic acid by dissolved silica. All readings were made at 18°C unless otherwise stated.

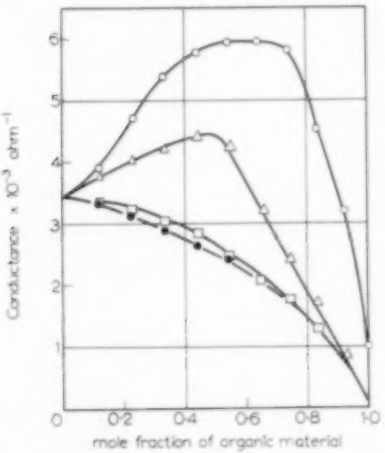

FIG. 1.—The influence of polyhydroxy compounds on the conductivity of pure molybdic acid: mole fraction—conductivity curves
□ Pentaerythritol
○ Gluconic acid
△ Erythritol
● Glycerol, glucose, fructose, salicin.

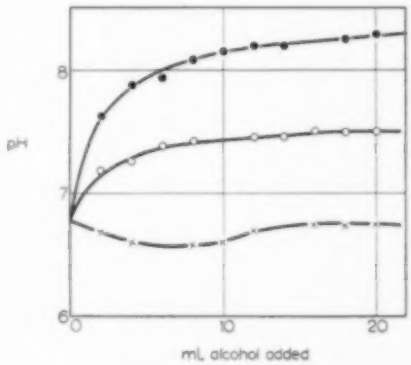

FIG. 2.—Influence of polyalcohols on the pH of "neutral" sodium molybdate
All contain 10 ml M/10 sodium molybdate with varying quantities of alcohol solution, made up to 30 ml with distilled water.
● Mannitol
○ Erythritol
× Glycerol

RESULTS AND DISCUSSION

(1) *Complex formation between polyhydroxy compounds and molybdic acid prepared by ion exchange*

In this investigation a series of tubes were prepared containing x ml of 0·085 M molybdic acid and $(50 - x)$ ml of 0·1 M polyhydroxy compound, where x was varied to cover a range of mole fractions from 0 to 1. The tubes were then shaken for 2 days to ensure complete formation of any complex, although separate experiments showed that where complex formation occurred, it was complete within 2 hr. The conductivity of the resulting solutions is shown in Fig. 1: the pH-mole fraction curves were similar in shape. From this figure it can be seen that gluconic acid and erythritol react with molybdic acid to form complexes with mole ratios 2 : 1 and 1 : 1, but a wide range of polyhydroxy compounds show no tendency to complex. Partial reduction of the molybdic acid to molybdenum blue occurs within 2 days only in the case of fructose, but this has no appreciable effect on the conductivity. Both of the complexes behave as strong acids. Addition of sodium hydroxide to the erythritol complex, for example, causes a decrease in conductivity to a Na : Mo ratio of 1 : 2; further addition causes a regular increase in conductivity to a ratio of

1 : 1, the conductivity becoming constant after the addition of each aliquot of sodium hydroxide. Equilibrium is established slowly after a ratio of 3 : 2; in some cases an interval of 20 min elapsed before equilibrium was attained after addition of an aliquot of sodium hydroxide. Titration of a similar quantity of acid at the same concentration in the absence of erythritol produced a break at the same Na : Mo ratio, but in this case equilibrium was established rapidly throughout the whole titration. This suggests that an erythritol complex of some form is stable to an Na : Mo ratio of 3 : 2 and decomposition occurs only after the addition of further sodium hydroxide.

(2) *Complex formation between polyhydroxy compounds and molybdic acid in "neutral sodium molybdate"*

Addition of mannitol to neutral sodium molybdate causes an increase in pH. This is claimed by SOUBAREW-CHATELAIN[7] to be due to the reaction

$$2Na_2MoO_4 + 2H_2O + C_6H_{14}O_6 = Na[Mo_2O_7(H{\cdot}C_6H_{14}O_6)] + 3NaOH$$

Little evidence exists to support the formulation of molybdic acid as $H_2Mo_2O_7$ but a displacement of the above type obviously occurs. This investigation was extended to include a wide range of polyhydroxy compounds and some of the results are shown in Fig. 2. At equimolecular concentration the mannitol complex is stronger than the erythritol complex but glycerol does not appear to form a complex. The effect of glucose, inositol, salicin and penta erythritol was also examined. These compounds do not affect the pH of aqueous sodium molybdate.

(3) *Complex formation between polyhydroxy compounds and commercial molybdic acid*

Complex formation between commercial molybdic acid containing ammonia and mannitol has been reported by FREY[6] who formulated it as

$$[Mo_2O_7HC_6H_{14}O_6NH_3]^-H^+$$

In the present investigation, complex formation between commercial molybdic acid of the same composition as that used by FREY[6] and a wide range of polyhydroxy compounds was examined. Complex formation was found between this acid and erythritol, gluconic, galactonic and arabonic acids (Figs. 3 and 4). No tendency to form complexes was shown by inositol, glycerol, penta erythritol, glucose or sucrose. Fructose showed a slight tendency to complex. The curve obtained on rapid conductometric titration of the erythritol complex showed some interesting features (Fig. 5) and for the purpose of comparison, that obtained on titration of the mannitol complex is also included. In equimolecular quantities mannitol affects* the acidity and conductivity of the molybdic acid more than erythritol. If excess of both materials is added, however, the conductivity and pH become equal. FREY has claimed that

* This molybdic acid solution was prepared by boiling 850 mg of molybdic acid (commercial) with distilled water, cooling then titrating 50 ml aliquots in the presence and absence of polyhydroxy compounds. Mannitol and erythritol always *decreased* slightly the conductivity of the solution prepared in this way although the pH of the solutions 3·58 alone, 3·32 in the presence of mannitol and erythritol are as expected.

In all other experiments using this material (e.g. Figs. 3 and 4) the solutions were prepared by agitation of the materials at 18°C and the presence of mannitol and erythritol increased the conductivity and decreased the pH.

[7] Z. SOUBAREW-CHATELAIN, *C.R. Acad. Sci., Paris* **208**, 1652 (1939).

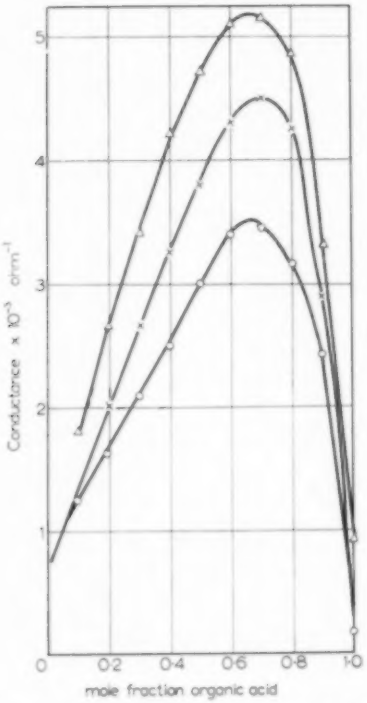

FIG. 3.—Complex formation between polyhydroxy organic acids and molybdic acid.
△ Gluconic
○ Galactonic
× Arabonic

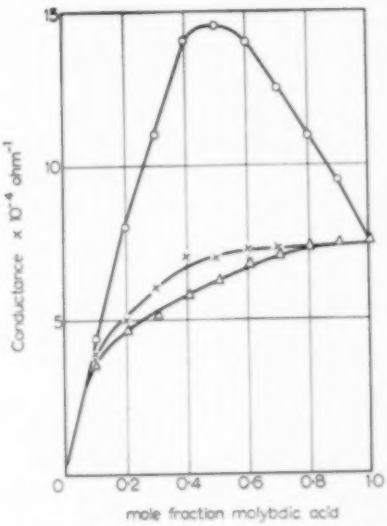

FIG. 4.—Influence of polyalcohols on the conductivity of molybdic acid.
○ Erythritol × Pentaerythritol
△ Glycerol, glucose, sucrose, inositol

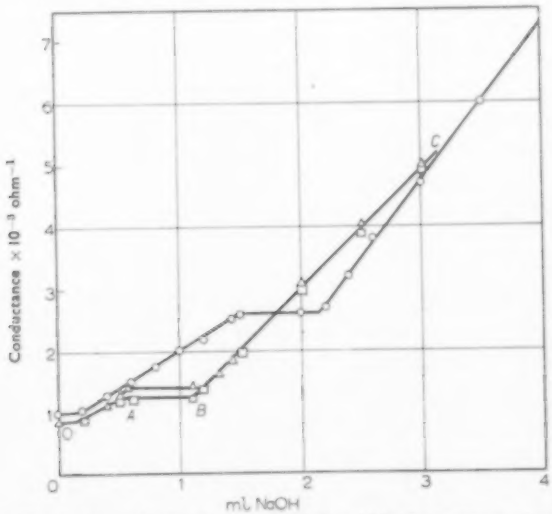

FIG. 5.—Conductometric titration of molybdic acid in the presence of polyalcohols.
○ Alone and in the presence of 500 mg glucose
△ 500 mg Erythritol added
□ 500 mg Mannitol added

the neutralization of the mannito complex proceeds in the following manner if sufficient time is allowed for equilibrium.

$$H[HMo_2O_7C_6H_{14}O_6NH_3] + NaOH = Na[HMo_2O_7C_6H_{14}O_6NH_3] + H_2O$$

$$Na[HMo_2O_7C_6H_{14}O_6NH_3] + 2NaOH = Na_2MoO_4 + NaNH_4MoO_4 + C_6H_{14}O_6 + H_2O$$

$$NaNH_4MoO_4 + NaOH = Na_2MoO_4 + NH_4OH$$

In Fig. 5 the initial neutralization *OA* proceeds rapidly as reported by FREY[6]. The second stage proceeds slowly and if the solution is allowed to reach equilibrium the curve obtained is similar in shape to that obtained in the absence of organic material. If the titration is conducted rapidly, however, the curve *OABC* (Fig. 5) is obtained in the presence of both mannitol and erythritol. Presumably in this case the ammonia is temporarily displaced from the complex and replaced by sodium and decomposition does not occur until the Na : Mo ratio is greater than 1 : 1. Unless great care is taken during this titration the resultant curve obtained is intermediate in shape between the two curves discussed.

In view of the similarity of the conductivity curves in the presence of erythritol and mannitol, it seems reasonable to suggest that if the ammonia is an integral part of the mannitol complex it is also an integral part of the erythritol complex. The erythritol complex ($2MoO_32C_4H_{10}O_4XH_2O{\cdot}NH_3$) contains twice as much organic material as the mannitol complex ($2MoO_3C_6H_{14}O_6XH_2O\ NH_3$). It has been shown in a previous paper that at the concentrations used in the present work molybdic acid is probably best formulated as $H_2Mo_4O_{13}$. Thus the equilibrium decomposition of the erythritol complex probably proceeds in the following stages, with the final decomposition of the organic complex occurring essentially at the latter part of the second stage

$$H_2[Mo_4O_{13}4C_4H_{10}O_42NH_3] + 2NaOH = Na_2[Mo_4O_{13}4C_4H_{10}O_42NH_3] + 2H_2O$$

$$Na_2[Mo_4O_{13}4C_4H_{10}O_42NH_3] + 4NaOH = 2Na_2MoO_4 + 2NaNH_4MoO_4 + 4C_4H_{10}O_4 + H_2O$$

$$2NaNH_4MoO_4 + 2NaOH = 2Na_2MoO_4 + 2NH_4OH$$

The erythritol and gluconic acid complexes both show most of the normal reactions of molybdate, e.g. MoS_3 is precipitated by passing hydrogen sulphide gas through a hot solution, acidified with hydrochloric acid and both give a yellow coloration with ammonium thiocyanate in acid solution. Although a brown precipitate is obtained by addition of potassium ferrocyanide to the gluconic acid complex, no precipitate is obtained from the erythritol complex.

The erythritol and the gluconic acid complexes have been crystallized from solution and examined by X-ray crystallography. Both complexes give definite patterns characteristic of the complex. It is difficult to obtain crystals of the gluconic acid complex but the erythritol complex crystallizes readily. The erythritol complex decomposes before melting during the range 170–175°. Several important conclusions may be drawn from the above results. Erythritol with hydroxyl groups on four adjacent carbon atoms reacts with molybdic acid to form a 1 : 1 complex, penta erythritol which also has four hydroxyl groups but arranged round a central carbon

atom exhibits little tendency to complex. Mannitol, a linear molecule with 6 hydroxyl groups on adjacent atoms can accommodate twice as much molybdic acid as erythritol, but inositol, a cyclic hexahydroxy alcohol, has no tendency to react. Glycerol with three hydroxyl groups on adjacent carbon atoms shows no tendency to complex in either acid or neutral solution. Thus it appears that molybdic acid, or molybdate ions complex only with linear polyhydroxy compounds containing four or more hydroxyl groups on adjacent carbon atoms. It is also of interest to note that glucose with an aldehyde group does not complex, whereas gluconic acid with a carboxyl group, which has a marked tendency to form an internal compound, complexes with molybdic acid. Complex formation between glycerol or glucose and molybdic acid has been reported by RIMBACH and LEY[1] but it appears from the above work that these substances have little tendency to react with molybdic acid in either acid or neutral solution. Fructose is reported to form a complex with ammonium molybdate,[8] whilst some tendency has been observed for such complexing with impure molybdic acid the extent is not appreciable. Pure molybdic acid shows no tendency to react with fructose.

Complex formation between polyhydroxy compounds and molybdic acid has complicated the colorimetric determination of many elements. The formation of heteropoly acids between molybdic and the oxy-ion of the element is an essential stage in the determination. The presence of an excess of polyhydroxy compound, which complexes with the molybdic acid present, inhibits the formation of the heteropoly acid. In the colorimetric determination of silica by a standard procedure,[9] as little as 70 mg of mannitol completely prevented the analytical determination. It is of interest to note, however, that not all of the compounds which complex with molybdic acid interfere with the analytical determination.

Acknowledgements—The author wishes to thank MR. H. BUCHWALD for some gravimetric determinations of molybdenum and MR. MCDONALD of the Atomic Energy Authority (Windscale Works) for the X-ray examination of the organic molybdate complexes.

[8] L. D. SCOTT, *J. Lab. Clin. Med.* **19**, 523 (1934).
[9] A. PRENTICE and P. D. RITCHIE, *J. Appl. Chem.* **6**, 21 (1956).

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TRI-*n*-BUTYL PHOSPHATE AS AN EXTRACTING AGENT FOR INORGANIC NITRATES—VI

FURTHER RESULTS FOR THE RARE EARTH NITRATES

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(*Received* 7 *July* 1958)

Abstract—Extraction of the higher lanthanide nitrates by tri-*n*-butyl phosphate (TBP) is generally similar to that of the lower lanthanides. However the trend of increasing extractability with atomic number in the lower sub-group (La–Gd) is not always continued in the higher sub-group (Gd–Lu). Moreover there is sometimes a slight discontinuity at the half-way point (Gd), and sometimes an appreciable difference between lanthanides of even and of odd atomic number. All the lanthanides appear to form tri-solvates $M(NO_3)_3 \cdot 3TBP$.

IT is a familiar idea that there is a steady gradation in properties along the lanthanide series. Experimental evidence for the gradation is however rather meagre, largely because well-characterized specimens of the later lanthanides have only become available fairly recently. Recent work has moreover brought to light certain irregularities in the progression from element to element.

Ion exchange and solvent extraction are particularly suitable techniques for studying the gradation. A change of 10 per cent in partition coefficient, which is usually readily measurable, corresponds to as little as 0·05 kcal in free energy, so that relatively small irregularities can be detected. Most such investigations hitherto have, however, been restricted to one or two sets of conditions, and few have included the entire series of lanthanides.

The present paper extends our earlier work[1] on the tri-*n*-butyl phosphate (TBP) extraction of traces of lanthanides to cover the complete series. Moreover all aqueous nitric acid concentrations from ca. 0·3–16 M have been studied with 100% TBP, as well as 15·6 M HNO_3 with 1–5% TBP diluted with "odourless" kerosene. This detailed investigation has brought to light a remarkably wide variety of behaviour.

At one time it appeared that extractability by TBP might be a steadily varying property along the lanthanide series, and PEPPARD *et al.*[2] proposed a logarithmic law

$$\log D = Z \log S + \text{constant} \qquad (1)$$

where D = partition coefficient, Z = atomic number, S = constant = separation factor (ratio of partition coefficients) for adjacent elements. As soon, however, as the higher lanthanides were studied at all extensively it became apparent that the law was not a general one; at the lower acidities, indeed, PEPPARD *et al.*[3] found that there was

[1] D. SCARGILL, K. ALCOCK, J. M. FLETCHER, E. HESFORD and H. A. C. MCKAY, *J. Inorg. Nucl. Chem.* **4**, 304 (1957).
[2] D. F. PEPPARD, J. R. FARIS, P. R. GRAY and G. W. MASON, *J. Phys. Chem.* **57**, 294 (1953).
[3] D. F. PEPPARD, W. J. DRISCOLL, R. J. SIRONEN and S. MCCARTY, *J. Inorg. Nucl. Chem.* **4**, 326 (1957).

a reversal in the trend of extractabilities after gadolinium. Our present work confirms this and has brought further phenomena to light, especially an alternation in extractability between elements of odd and even atomic number.

These effects do not seem to be due to changes in the molecular composition of the species extracted. Our data for extraction with 1–5% TBP in kerosene indicate that all the lanthanide nitrates form trisolvates, $M(NO_3)_3 \cdot 3TBP$. (PEPPARD *et al.*,[3] however, rather cautiously propose $[M(TBP)_a(H_2O)_{x-a}](NO_3)_3$ "in which x is probably 6", and a varies with acidity and atomic number, but we find their argument for this formula unsatisfactory.)

EXPERIMENTAL

The partition coefficients were determined by the method described in Part I of this series,[4] the rare earth concentrations being <1 g/l. It was however found desirable to increase the stirring times, sometimes to as much as 60 min, when the partition coefficients (organic/aqueous) were very low. All the measurements were made in a thermostat at 25°C.

Radioactive tracers were used throughout. Carrier-free ^{91}Y, ^{144}Ce and ^{147}Pm were supplied by the Radiochemical Centre, Amersham. All others, viz. ^{140}La, ^{142}Pr, ^{147}Nd, ^{153}Sm, $^{152,154}Eu$, ^{159}Gd, ^{160}Tb, ^{165}Dy, ^{166}Ho, ^{169}Er, ^{170}Tm, ^{175}Yb and ^{177}Lu, were prepared by pile irradiation at Harwell. In most cases the spectroscopically pure oxides were used. ^{147}Nd and ^{159}Gd of high specific activity were, however, prepared by irradiating separated isotopes supplied by the E.M. Separator Group at Harwell; 87% ^{146}Nd and 97% ^{158}Gd were used. In some instances short-lived radioactive impurities were allowed to decay away before the tracers were used; this was especially the case with ^{147}Nd and $^{152,154}Eu$.

The radiochemical purity of the tracers was checked in all cases by γ-spectrometry, and sometimes by β-ray absorption plots. No radioactive impurities were found which had originated from chemical impurities in the irradiated material, but in two cases there were significant impurities due to nuclear side-reactions. These were ^{147}Nd, which contained ^{147}Pm, and ^{169}Er, which contained ^{171}Tm. (Short-lived impurities had been allowed to decay.) The ^{147}Nd was dealt with simply by measuring it through sufficient aluminium to absorb the weak β-rays of ^{147}Pm. In the ^{169}Er case the counting trays were remeasured after 100 days, when only ^{171}Tm was left, and the initial results could then be corrected.

RESULTS AND DISCUSSION

Effect of varying the TBP *concentration: Formulae of the* TBP*-solvates*

In the present series of papers, the evidence has always tended to indicate a definite number of TBP molecules attached to each metal nitrate molecule in the TBP phase, equal to two for nitrates of the general formulae $M(NO_3)_4$ and $MO_2(NO_3)_2$, and equal to three for $M(NO_3)_3$. There has been no sign of the solvation varying with, for example, acidity; or, in the lanthanide series with atomic number. Our evidence comes principally from partition experiments at low and varying TBP concentrations, with a constant aqueous phase; but it is supported in some instances by other lines of reasoning.[5]

Because an alternative view has recently been presented,[2] we have taken pains to establish the limiting power law for the lanthanides at low TBP concentrations as definitely as possible. A selection of our results is shown in Fig. 1; entirely comparable results have been obtained for yttrium and the remaining lanthanides (Ho, Er, Tm, Yb and Lu) and also for thulium with aqueous phases of the following compositions: 0·084 M HNO_3, 4 M $NaNO_3$; 1 M HNO_3, 6 M $NaNO_3$; 0·072 M HNO_3, 7 M $NaNO_3$. It appears that in all cases the limiting law is a cubic, corresponding to the formation

[4] K. ALCOCK, F. C. BEDFORD, W. H. HARDWICK and H. A. C. MCKAY, *J. Inorg. Nucl. Chem.* **4**, 100 (1957).
[5] T. V. HEALY and H. A. C. MCKAY, *Trans. Faraday Soc.* **52**, 633 (1956).

of a trisolvate, $M(NO_3)_3 \cdot 3TBP$. There is no indication of any change in solvation number with either atomic number or (at least in the case of thulium nitrate) acidity.

Our experiments have generally been carried out in the range 1–5% TBP in diluent. It would be desirable to go to higher dilutions still, but it is difficult to make accurate measurements of partition coefficients which are smaller than say 10^{-4}. Even in the 1–5% range, results at low acidities can only be obtained in presence of a salting-out agent (e.g. sodium nitrate); however, this makes no difference to the principle of the method, though it does involve rather careful work to ensure that the final aqueous acidity remains constant throughout the series of partitions.

The slopes actually observed, e.g. in Fig. 1, differ slightly from three. This, we believe, is due to deviations from ideal behaviour in the organic phase. Such deviations

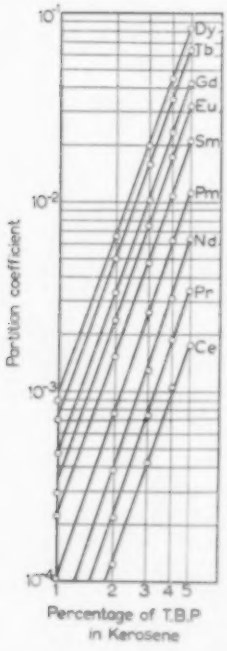

FIG. 1.—Extraction of rare earths by 1–5% TBP in kerosene from 15·6 M HNO_3 (aqueous).

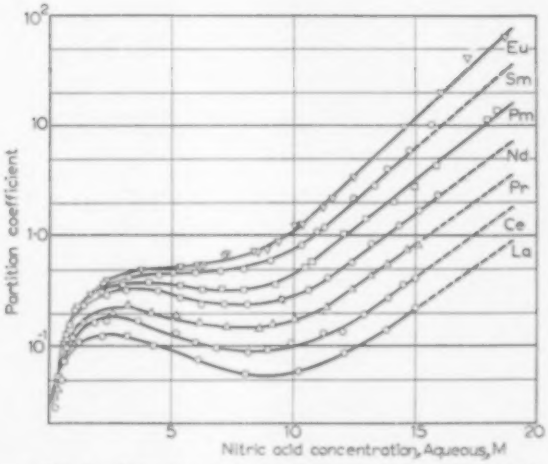

FIG. 2.—Extraction of the lower lanthanides by 100% TBP.

might be expected to give rise to slopes lying between about 2·7 and 3·1 instead of 3 for 5% TBP, and the observed slopes fall well within these limits.[6]

At higher TBP concentrations, however, non-ideality may completely obscure the situation, and slopes widely different from the true limiting slope of 3 may be found. For this reason we do not feel that PEPPARD *et al.* results with 25–100% TBP in carbon tetrachloride[3] can be used to establish solvation numbers. It should be noted, however, that we do not dispute the square, cube and fourth-power laws they have observed under different conditions; we have ourselves obtained a variety of different power laws at high TBP concentrations. We would also like to point out that such

evidence as is available supports the formation of anhydrous rather than hydrated complexes.[5]

Effect of varying the acidity

The curves in Figs. 2–4 are based on the results in Table 1 and in Part II[1] of this series. In considering the lower lanthanides in Part II we had sometimes to depend on not entirely satisfactory data from other sources, but this is no longer necessary, and Fig. 2 should therefore be more reliable than the corresponding diagram in Part II. Of the higher lanthanides, some have been investigated here for the first time.

There are no serious discrepancies with other workers' results, e.g. those of PEPPARD *et al.*,[3] and of GRAY and THOMPSON,[7] in addition to those quoted in Part II. Our results are, however, more comprehensive and often show less scatter; fresh details have come to light in consequence, though the broad outlines of the picture remain unchanged.

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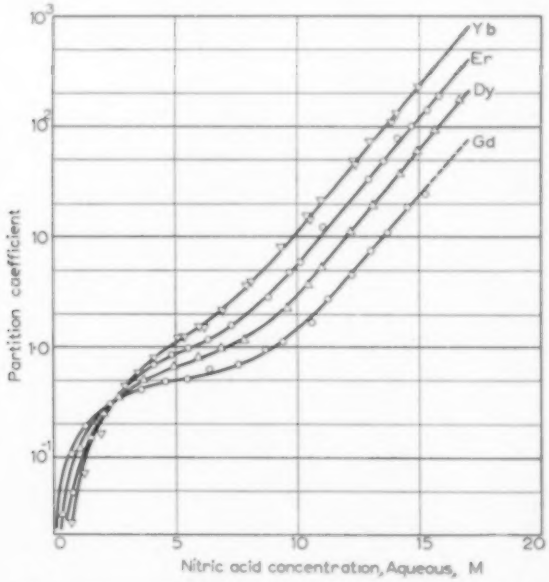

FIG. 3.—Extraction of the even-Z higher lanthanides by 100% TBP.

The curves are of the shapes familiar from earlier papers in this series. It is interesting to note the gradation from the lanthanum curve, which resembles that of, for example, thorium, to the lutecium curve, which resembles that of zirconium. The shapes can be explained in accordance with the general principles given by HESFORD and MCKAY[6] and mentioned briefly in Part II, but there is not enough information, e.g. on nitrate complexing, for quantitative calculations.

The existence of common points on the curves in Figs. 3 and 4, at $D = 0{\cdot}30$, 2·3 M HNO_3 and $D = 0{\cdot}65$, 4·9 M HNO_3 respectively, is worthy of note. There may

[6] E. HESFORD and H. A. C. MCKAY, *Trans. Faraday Soc.* **54**, 573 (1958).
[7] P. R. GRAY and S. G. THOMPSON, *UCRL*-2069 (1952).

also be a common point in Fig. 2 at about $D = 0{\cdot}06$, 0·4 M HNO_3, but we have not investigated the region below 1 M HNO_3 very carefully.

Separation factors

Fig. 5 shows three separation factor curves, based on Figs. 2–4. The three pairs of elements have been chosen as characteristic of the lower lanthanides, the even-Z

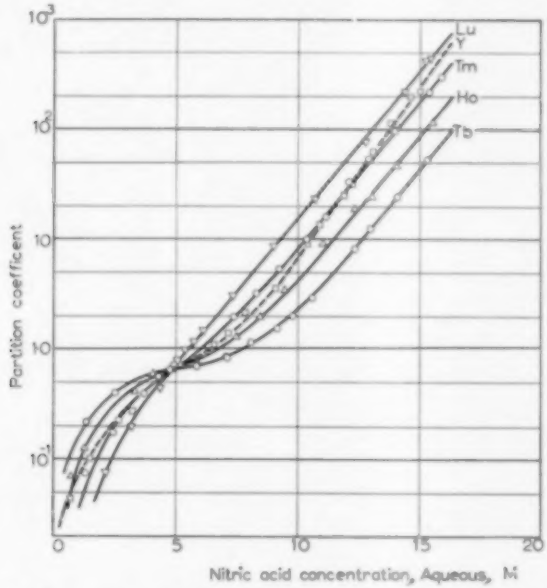

FIG. 4.—Extraction of yttrium and the odd-Z higher lanthanides by 100% TBP.

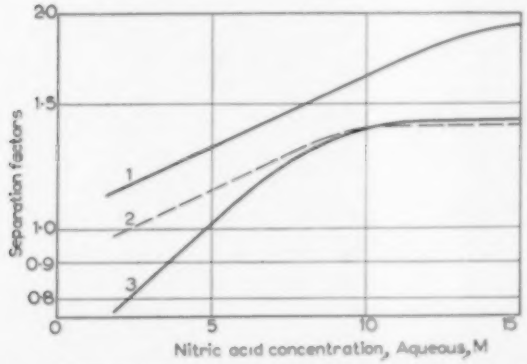

FIG. 5.—Separation factors 1. $(D_{Eu}/D_{Pr})^{1/4}$ 2. $(D_{Yb}/D_{Dy})^{1/4}$ 3. $(D_{Lu}/D_{Tb})^{1/6}$.

higher lanthanides and the odd-Z higher lanthanides respectively. The appropriate fourth or sixth root has been taken in each case, to reduce all the curves to the same basis: if equation (1) held strictly we should then be dealing with the quantity S, and the curves would be of general significance. In fact, however, equation (1) is never more than an approximation, and for the lower lanthanides below about 6 M HNO_3 (aqueous) it fails altogether.

Table 1
(100% TBP throughout)

HNO_3 conc. (aq.) (M)	Partition coefficient (org./aq.)	HNO_3 conc. (aq.) (M)	Partition coefficient (org./aw.)	HNO_3 conc. (aq.) (M)	Partition coefficient (org./aq.)
Praseodymium		Neodymium		Promethium	
0·34	0·041	0·53	0·050	0·36	0·053
1·38	0·164	0·86	0·158	0·70	0·127
2·58	0·20	1·40	0·23	1·18	0·22
3·20	0·22	2·36	0·29	2·16	0·31
4·13	0·20	3·12	0·32	2·99	0·36
5·20	0·191	4·47	0·33	4·04	0·39
6·16	0·167	5·31	0·28	5·37	0·36
7·23	0·152	6·22	0·24	6·27	0·34
8·54	0·146	7·16	0·24	7·03	0·33
9·12	0·159	8·09	0·24	7·94	0·33
10·0	0·175	9·53	0·27	9·24	0·37
11·3	0·23	10·6	0·33	10·4	0·53
12·4	0·33	11·4	0·42	10·8	0·57
13·2	0·44	12·4	0·58	12·0	1·03
13·8	0·56	13·2	0·85	13·0	1·41
14·7	0·75	14·3	1·25	14·1	2·0
15·1	0·83	15·1	1·70	14·9	2·8
		15·9	2·3	15·8	4·3
				17·9	11·4
				18·4	13·2
Samarium		Gadolinium		Terbium	
0·59	0·077	0·72	0·108	1·36	0·21
1·04	0·21	1·29	0·193	2·55	0·39
2·24	0·38	2·31	0·31	4·29	0·57
3·25	0·42	2·94	0·37	4·95	0·70
4·48	0·44	3·56	0·42	5·80	0·72
5·06	0·46	4·58	0·49	5·83	0·73
5·96	0·45	5·47	0·52	7·05	0·87
7·01	0·46	6·40	0·63	7·10	0·85
7·97	0·50	7·54	0·70	8·10	1·19
9·04	0·60	8·67	0·95	9·15	1·55
10·3	0·83	9·40	1·14	9·77	2·0
11·0	1·08	10·6	1·70	10·6	3·0
11·3	1·16	11·2	2·8	12·3	8·2
12·5	2·2	12·2	4·6	13·0	12·7
13·3	2·8	13·0	7·6	14·1	24
13·9	4·1	13·7	11·0	15·3	53
14·7	5·9	14·5	18·5		
15·7	10·4	15·3	25		

TABLE 1—*continued.*

HNO_3 conc. (aq.) (M)	Partition coefficient (org./aq.)	HNO_3 conc. (aq.) (M)	Partition coefficient (org./aq.)	HNO_3 conc. (aq.) (M)	Partition coefficient (org./aq.)
Dysprosium		Holmium		Erbium	
0·30	0·031	0·72	0·071	0·39	0·028
0·78	0·084	1·23	0·129	0·79	0·048
1·09	0·123	3·31	0·42	1·51	0·149
2·05	0·25	4·10	0·60	2·05	0·25
2·64	0·35	5·15	0·73	3·46	0·58
3·67	0·51	7·47	1·30	4·10	0·70
4·90	0·67	8·47	1·99	4·85	0·88
5·90	0·83	9·45	3·5	4·89	0 83
6·84	0·99	11·1	9·3	5·51	1·00
7·78	1·16	12·3	19·1	6·33	1·18
9·54	2·3	13·0	24	6·57	1·31
10·5	3·7	14·0	47	7·30	1·58
11·0	5·3	15·5	117	8·81	2·9
12·1	11·1			9·67	4·8
13·1	19·5			10·1	6·1
14·2	38			11·0	12·2
14·9	61			12·9	33
15·6	93			13·5	48
16·6	174			14·1	68
				14·7	99
				15·3	137
				15·8	186
				18·0	770
Thulium		Ytterbium		Lutecium	
0·58	0·027	0·33	0·0087	0·52	0·0133
1·28	0·076	0·69	0·026	1·03	0·034
2·43	0·17	1·26	0·073	1·56	0·060
2·72	0·23	1·95	0·163	2·17	0·075
3·70	0·39	2·92	0·42	3·23	0·198
4·74	0·65	2·98	0·41	4·36	0·44
7·38	2·0	3·90	0·71	4·73	0·63
8·30	3·2	4·12	0·79	5·08	0·77
9·22	5·4	5·13	1·20	5·38	0·96
10·4	10·0	5·34	1·23	5·75	1·17
11·1	16·2	5·96	1·53	6·16	1·48
12·1	34	6·21	1·52	7·35	3·1
12·9	54	6·95	2·1	9·03	8·6
13·0	52	7·99	3·6	10·8	24
14·0	97	8·10	4·0	12·8	77
14·0	100	9·36	8·2	14·4	220
15·4	210	10·4	15·4	15·2	420
15·9	300	10·6	14·5	15·5	450
		11·0	22		
		12·3	49		
		12·4	46		
		13·0	74		
		13·9	109		
		14·1	132		
		15·0	220		
		17·3	920		

For satisfactory separations, separation factors as different as possible from unity are desirable. Fig. 5 therefore indicates good conditions to use, and shows that the higher lanthanides are more difficult to separate than the lower.

Variation of extractability with atomic number

Certain irregularities can be observed in the sequence of curves in Figs. 2–4. These can best be demonstrated by plotting partition coefficients for a given set of conditions against atomic number, as in Figs. 6 and 7. If the logarithmic law, equation (1), held, these plots would all be straight lines, but it is obvious that the situation is far more complex than this.

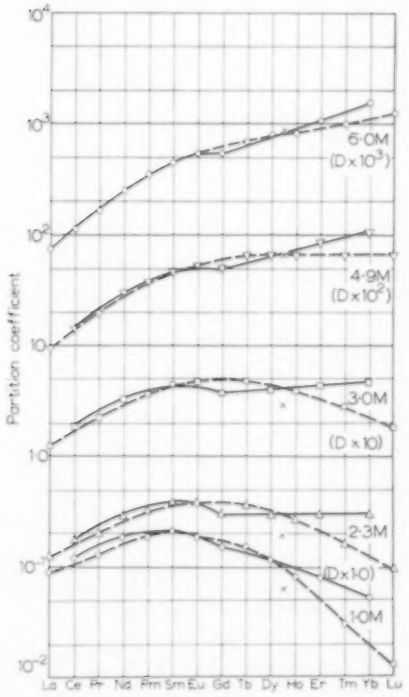

FIG. 6.—Partition coefficient as a function of atomic number. × Yttrium

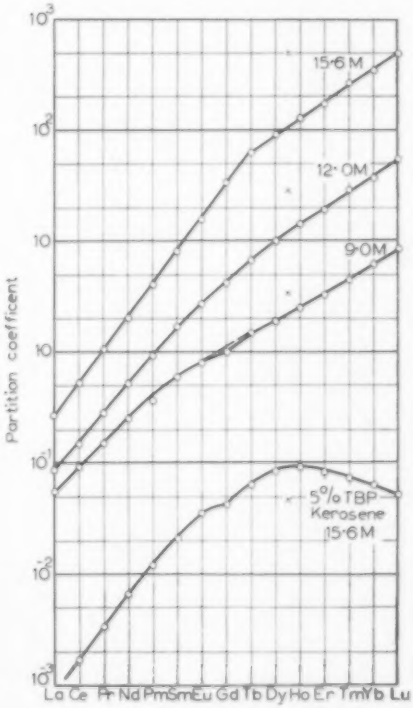

FIG. 7.—Partition coefficient as a function of atomic number. × Yttrium

In an attempt to extend the logarithmic law, PEPPARD *et al.*[3] drew attention to the change in direction of the curves around gadolinium, and suggested that the data might be fitted by two straight lines. Each line would obey equation (1), but with different slopes for the lower and higher lanthanide branches. The two branches would intersect at gadolinium, the element for which the 4*f* shell is half-filled. This again is clearly too simple a picture, however, and even PEPPARD *et al.* own plots often suggest a continuous curve rather than two straight lines, if examined with an unprejudiced eye.

The full results, indeed, give only limited support to the idea that gadolinium represents a turning-point. At 15·6 M HNO_3 (aqueous) with 100% TBP, for example,

there is a well-marked turning-point, but it occurs at terbium, and in many other cases there is no very definite turning-point at all.

Nevertheless, there is often a singularity at the mid-point element, gadolinium. This appears most simply in the two lowest curves in Fig. 7, where gadolinium appears to be 10 or 20 per cent less extractable than might be expected from the behaviour of neighbouring elements. The effect is a fairly small one, but lies well outside our probable experimental error; moreover the 5% TBP curve is based not on single determinations but on a consistent series in the range 1–5% TBP in kerosene.

At the lower acidities another new effect appears, namely, a separation of the curves into odd-Z and even-Z branches. This lies even further outside our probable error than the gadolinium effect, and is particularly apparent among the higher lanthanides. Our impression is furthermore that a single smooth curve can always be drawn through the points for the odd-Z elements, but that there is often a discontinuity at gadolinium among the results for the even-Z elements.

The fact that the common points are different in Figs. 3 and 4 demonstrates the odd-even effect in another form.

Comparison of extractability with other properties

Diagrams have already appeared in the literature, comparable to Figs. 6 and 7, showing the variation of other lanthanide properties with atomic number. The most fundamental of these is for the ionic radii of the tripositive ions,[8] which decrease smoothly from lanthanum to lutecium. SURLS[9] has noted that the Gd^{3+} radius lies about 0·002 Å above a curve through the remaining points, but as the estimated error is usually $\pm$0·005 Å, this is of doubtful significance.

Many other properties do, however, show a definite break at gadolinium, similar to those in Fig. 7. Fig. 8 gives plots of several sets of results from the literature illustrating this. In certain cases, too, gadolinium represents a turning-point: nitrate and bromate solubilities, for example, fall from lanthanum to gadolinium and then rise again. There are, on the other hand, properties which show no singularity at gadolinium, e.g. sulphate solubilities.

Only one series of results indicates any odd-even effect, namely those due to SURLS[9] on lanthanide adsorption on Dowex-50 from 0·110 M $HClO_4$ at 25° (Fig. 9). Here, though SURLS makes no comment, there seems to be a definite odd-even effect between neodymium and holmium with an anomaly among the three elements at the beginning of the series.

The position of yttrium

The position of yttrium now appears much less of an anomaly than it did when Part II was written. It behaves generally like a higher lanthanide of odd- rather than even-Z. In comparison with the odd lanthanides, however, it behaves as if its atomic number slowly varied, and Fig. 10 shows how its apparent atomic number varies with acidity. From its ionic radius we should expect an apparent atomic number of almost exactly 67, corresponding to holmium. In Figs. 6 and 7 it has been plotted at $66\frac{1}{2}$.

The rather low apparent atomic number of yttrium at low nitric acid concentrations

[8] D. H. TEMPLETON and C. H. DAUBEN, *J. Amer. Chem. Soc.* **76**, 5237 (1954).
[9] J. P. SURLS, *UCRL*-3209 (1956).

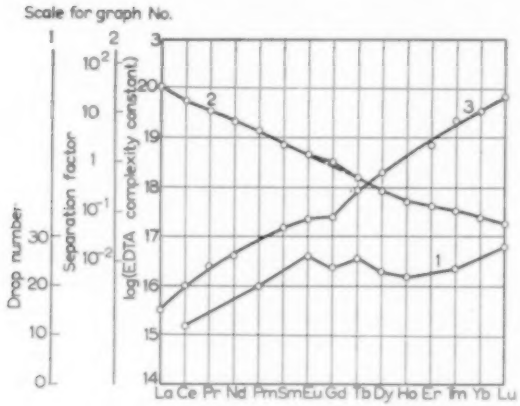

FIG. 8.—Miscellaneous properties.
1. Elution from Dowex-1 with ammonium thiocyanate[10]
2. Elution from Dowex-50 with ammonium alpha-hydroxy-*iso*butyrate[11]
3. EDTA-complexing constants at 20°C in 0·1 M KNO_3[12]

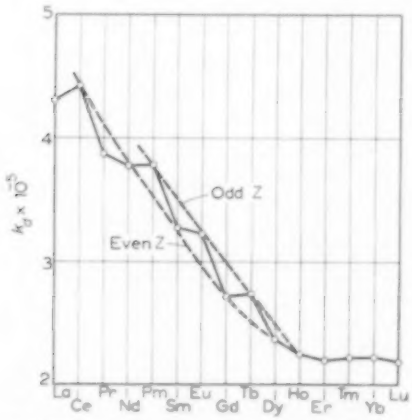

FIG. 9.—Adsorption on Dowex-50 from 0·110 M perchloric acid.[9]

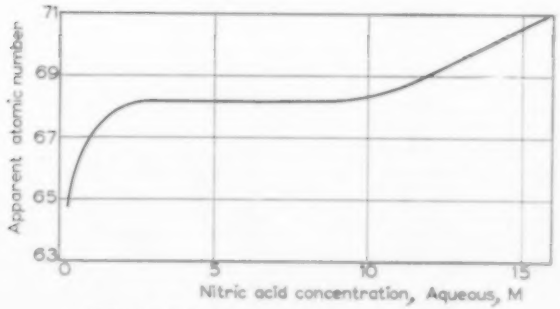

FIG. 10.—Yttrium as an odd-*Z* pseudo-lanthanide.

[10] J. P. SURLS and G. R. CHOPPIN, *J. Inorg. Nucl. Chem.* **4**, 62 (1957).
[11] G. R. CHOPPIN and R. J. SILVA, *J. Inorg. Nucl. Chem.* **3**, 153 (1956).
[12] G. SCHWARZENBACH, R. GUT and G. ANDEREGG, *Helv. Chim. Acta* **37**, 938 (1954).

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is in line with its behaviour in complexing with EDTA and on ion exchange columns at low acidities, when it often appears in the neighbourhood of dysprosium (no. 66) or even terbium (no. 65).

Some theoretical observations

In the present state of our knowledge it is impossible to give a full explanation covering all the varied features of the results, but a few general observations may be made:

(1) The complexity of the phenomena is presumably a reflection of the complexity of the processes occurring during extraction. In addition to transport across the interface, we have to consider complexing by three different ligands (NO_3^-, H_2O and TBP), as well as quite drastic changes in the solvent media.

(2) The full complexity may be missed if too restricted a range of experiments is carried out, and undue attention may be paid to what are in reality unimportant features. In Fig. 9, for example, there is a change in trend at terbium, but in the light of all the results presented here, this seems of limited significance.

(3) The ionic radius plays a major part in determining behaviour, as is evidenced by the yttrium results and the slow gradation through the lanthanide series. Nevertheless many properties show a reversal in trend at some point along the series ("non-monotonic ordering"), though not necessarily at the half-way point, gadolinium. Such reversals may be due to a varying balance between two or more competing factors.

(4) Ionic deformability is presumably a further factor of significance.

(5) Effects in the organic as well as the aqueous phase are significant, despite the fact that the metal always exists almost exclusively as $M(NO_3)_3 \cdot 3TBP$ in the organic phase. The difference in the curves in Fig. 7 for 5% TBP in kerosene and 100% TBP demonstrates this.

(6) A singularity is observed fairly generally at gadolinium, and there must be a general explanation for it. Presumably the singularity is related to the fact that the 4*f* shell is half-full in the Gd^{3+} ion. Special explanations, such as the steric one put forward by WHEELWRIGHT *et al.*[13] for their series of EDTA complexity constants cannot apply to the gadolinium effect in general.

(7) The odd-even effect seems quite definite, but it is difficult to see an electronic reason for it. An odd-even effect would arise if, in building up the 4*f* shell, every second electron paired with the previous electron; but it is not believed that the shell builds up in this way.

Acknowledgements—The authors would like to acknowledge their indebtedness to the earlier work of Dr. A. H. S. MATTERSON and Miss J. A. TOWERS, which has however been superseded by the more accurate results given here.

[13] E. J. WHEELWRIGHT, F. H. SPEDDING and G. SCHWARZENBACH, *J. Amer. Chem. Soc.* **75**, 4196 (1953)

J. Inorg. Nucl. Chem., 1959, Vol. 9, pp. 290 to 301. Pergamon Press Ltd. Printed in Northern Ireland

OXIDATION STATES AND COMPLEX IONS OF URANIUM IN FUSED CHLORIDES AND NITRATES*

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(*Received* 14 *August* 1958)

Abstract—Oxidation states of uranium in fused LiCl–KCl eutectic, pyridinium chloride, and $LiNO_3$–KNO_3 eutectic were characterized spectrophotometrically. The (III), (IV) and (VI) oxidation states of uranium are stable in LiCl–KCl eutectic. The (IV) and (VI) oxidation states have been observed in pyridinium chloride. In $LiNO_3$–KNO_3 eutectic the (III) and (IV) states are oxidized to the (VI) oxidation state.

It was found that Al as well as U metal reduces U(IV) to U(III) while Mg metal reduces U(III) to U(O) in LiCl–KCl eutectic. On the basis of these experiments the U(III)-U(O) standard potential versus a 1 M Pt reference electrode can be predicted to lie between −1·77 and −2·58V. The U(IV)-U(III) potential versus the same electrode can be expected to be more positive than −1·77 V.

Spectrophotometric evidence indicates that U(IV) changes its co-ordination number from six to eight in going from fused pyridinium chloride to LiCl–KCl eutectic. Changes were observed in the UO_2(II) spectrum on addition of chloride ion to UO_2(II) solutions in $LiNO_3$–KNO_3 eutectic which were correlated with the formation of chlorocomplexes of uranyl ion.

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SINCE fused salts constitute the largest class of non-aqueous inorganic solvents, the development of a solution chemistry in fused salts should become a fruitful and fascinating area of inquiry.

Basic to an understanding of solution chemistry in fused salt solvents as in all other solvent systems is information pertaining to the oxidation states and oxidation–reduction behaviour of the solute ions. Information about the kinds and stabilities of complex ions is equally important because of the profound effects such complexes may have on oxidation–reduction potentials and other chemical properties of the solute ions.

Absorption spectrophotometry has been one of the classic tools in elucidating the chemistry of aqueous solutions, and it appears from our studies that this technique is promising for exploring the chemistry of fused salt solutions as well.[1–3]

In this paper results of studies of uranium dissolved in fused chlorides and nitrates are presented. Subsequent communications will deal with studies on other metal ions dissolved in fused salts.

EXPERIMENTAL

Spectrophotometer and furnace

A general problem to be encountered in making spectrophotometric measurements at temperatures above 500°C is due to the emission of black body radiation from the sample and container.

This problem is serious at higher temperatures because in most commercially available spectrophotometers, light from the source passes first through the monochromator, then through the sample

* Based on work performed under the auspices of the U.S. Atomic Energy Commission.

[1] D. M. GRUEN, *Nature, Lond.*, **178**, 1181 (1956).
[2] D. M. GRUEN, *J. Inorg. Nucl. Chem.* **4**, 74 (1957).
[3] D. M. GRUEN, P. GRAF and S. FRIED, *Proc. XVIth Int. Congress Pure and Appl. Chem.* p. 319, July (1957).

before finally striking the phototube. In these instruments, therefore, the phototube "sees" all of the black body radiation from the hot sample, in addition to the monochromatized beam. The signal (monochromatized beam) to noise (black body radiation) ratio rapidly diminishes with increasing temperature and is apparently low enough at 550°C to make quantitative spectrophotometric measurements difficult.[4,5]

Quantitative spectrophotometric measurements have now been made up to 850°C, by simply reversing the positions of light housing and phototube. With this arrangement, both the light from the source and the black body radiation from the sample pass through the monochromator before striking the phototube. Thus, the black body radiation problem is overcome until the sample temperature approaches the light source temperature. The Beckman DU spectrophotometer was chosen

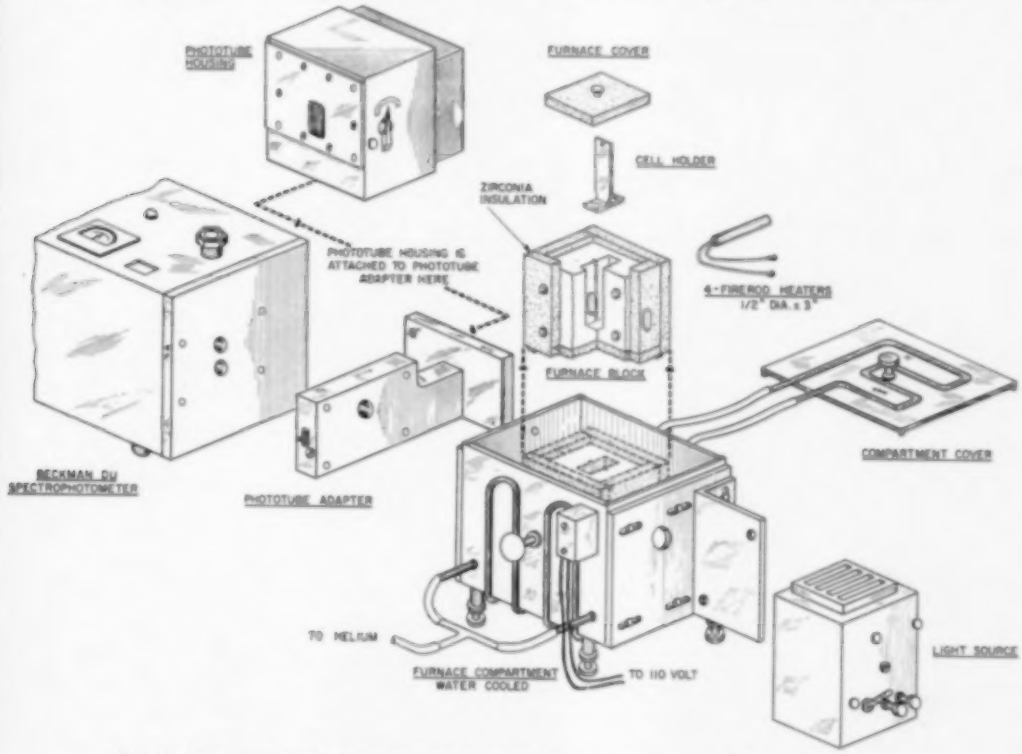

FIG. 1.—Beckman DU spectrophotometer adapted for measurements of absorption spectra at high temperatures.

for this work since fortunately it is designed so that repositioning of light source and detector is very easily accomplished.

The usual Beckman cell compartment was replaced by a water-cooled box which could be flushed with an inert gas during experiments. An exploded view of the #310 stainless steel furnace block situated in the box is shown in Fig. 1. The block (3 in. long × 3½ in. wide × 3 in. high) was machined to accommodate two 1 cm optical cells and was equipped with a handle for moving first one cell and then the other into the light path. Holes sunk horizontally into the block held four "Firerod" ½ in. heaters. The sides were insulated with ½ in. thick zirconia plates. Temperature control to ±1° was achieved with an electronic thermocouple control circuit and temperatures were measured with a thermocouple in close proximity to the sample.

Absorption spectra were measured in the range 300–1200 mμ and from 150°C to 850°C.

[4] B. R. SUNDHEIM and J. GREENBERG, *Rev. Sci. Instrum.* **27**, 703–704 (1956).
[5] B. R. SUNDHEIM and J. GREENBERG, *J. Chem. Phys.* **66**, 1056 (1958).

Preparation of samples

A. LiCl–KCl *eutectic.* Much of the work to be described was done with solutions of uranium in LiCl–KCl mixtures with composition close to that of the eutectic (about 59 mol % LiCl, m.p. about 350°). In order to obtain clear uranium solutions, free of oxidation and precipitation products, the eutectic had to be anhydrous.

Since water has an appreciable solubility in the eutectic even at 500°C[6] it is very difficult to achieve complete dehydration by vacuum fusion alone. Various techniques have been described for preparing anhydrous melts which involve treatment with HCl gas.[5,7,8]

The method developed during the course of the present study also involves bubbling HCl through the melt and has the additional advantage of furnishing an easily handled supply of anhydrous eutectic pellets. This method is best described by reference to Fig. 2.

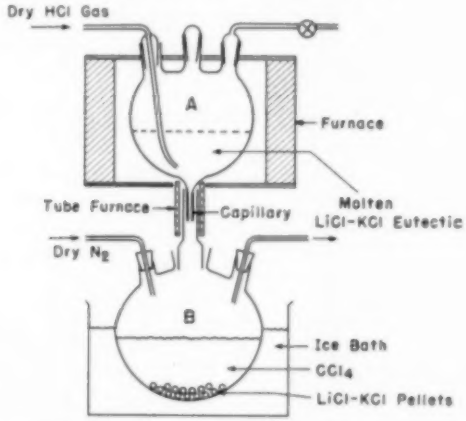

FIG. 2.—Apparatus for preparing anhydrous LiCl–KCl eutectic pellets.

A flask filled with a mixture approximating the eutectic composition of reagent grade LiCl and KCl was heated in a furnace to the melting point of the mixture. Tank HCl gas was bubbled through the melt for 2 hr. After this treatment a capillary tube attached to the bottom of the flask was heated to allow the molten eutectic to flow through it and to fall dropwise into a lower flask filled with CCl_4.

The rate of flow of the eutectic through the capillary and the size of the resulting pellets was controlled either by varying the diameter of the capillary or by changing the pressure above the melt. Although the density of liquid CCl_4 is slightly less (1·59 g/cm³ at 25°C) than that of the eutectic (1·69/cm³ at 400°C), the molten drops remained suspended at first on the surface of the CCl_4 presumably because they were enveloped by CCl_4 gas. After an outer crust of solidified eutectic had formed, the drops sank to the bottom of the flask. In this way kilogram quantities of evenly sized pellets of eutectic were prepared and were stored under CCl_4 until ready for use. Since the pellets did not adhere to one another, varying amounts could easily be withdrawn from the flask.

There were two contaminants in the pellets: dissolved HCl and occluded CCl_4. As will be described further on, filling of the optical cells was done on a vacuum line. In the course of this operation the HCl as well as the CCl_4 was pumped off and the small amount of C formed by pyrolysis of CCl_4 was removed by filtering the melt through a sintered fused silica disk.

Rectangular fused silica cells with a 10 mm light path were used for the optical work. The cells were attached to ½ in. × 18 in. fused silica tubes having several constrictions. Solutions were prepared and the cells were filled on a vacuum line. In general, a blank cell was filled with eutectic alone by melting approximately 8 g of eutectic pellets placed above a sintered fused silica disk of medium porosity which was situated in the uppermost section of the fused silica tube. The melt was made to flow through the disk into the cell by pressurizing the system with a few mm of He gas. Filtration

[6] W. J. BUCKHARD and J. D. CORBETT, *J. Amer. Chem. Soc.* **79,** 6362 (1957).
[7] H. A. LAITINEN, W. S. FERGUSON and R. A. OSTERYOUNG, *J. Electrochem. Soc.* **104,** 516 (1957).
[8] C. R. BOSTON and G. P. SMITH, *J. Phys. Chem.* **62,** 409 (1958).

through the disk usually resulted in a clear melt. Evacuation was continued at a pressure of 10^{-5} mm Hg until most of the dissolved HCl had been removed as evidenced by the cessation of bubble formation. The cell was then sealed off on the vacuum line from the upper section of the fused silica tube and placed in the heated spectrophotometer block.

The sample cell was filled in exactly the same manner as the blank cell except that an appropriate quantity (1–100 mg) of the desired uranium compound was placed in the cell first. It was important to use anhydrous compounds and to make all transfers involving these substances in a dry box.

After the spectra had been obtained, the cell was removed from the spectrophotometer and turned upside down to transfer the solution to the remaining circular section of quartz tubing which now served as a storage compartment. There the melt was allowed to solidify. To carry out analyses, the storage section was broken off from the cell proper and the salt column, which in general was free of the surrounding walls, extracted from it. The cell itself was then cleaned and re-used for the next experiment. Cells filled with eutectic prepared in the manner described above were not etched even when kept at temperatures of 850°C for several hours.

Standard chemical analyses for uranium were performed on weighed salt samples dissolved in aqueous solutions. Values of molar extinction coefficients were calculated using the analytically determined uranium concentrations together with the densities of the fused LiCl–KCl mixtures at the temperature of the measurements. The density of the uranium molten salt solutions was taken to be the density of the pure molten salt. The error in this assumption is probably small compared with other experimental errors since the uranium concentrations did not exceed about 0·01 M. Densities for the LiCl–KCl mixtures were obtained from the work of VAN ARTSDALEN and YAFFEE by interpolation of results these workers obtained on LiCl–KCl mixtures close to the eutectic composition.[9] It is estimated that the absolute values of the extinction coefficients are within 5 per cent of the values determined in the course of this work.

B. *Pyridinium chloride*. Eastman's Practical Grade pyridinium chloride was purified by two fractional distillations in a Pyrex system. The melting point of the product was 144 ± 1°C. The main impurities of the Practical Grade product are water and free pyridine. Pyridinium chloride prepared in this way does not discolour when heated to 200°C for 6 hr in a sealed tube. Melts kept above this temperature for two or three days show a slightly yellow colour which changes to brown on continued heating presumably because of decomposition of the pyridine ring. The relatively high vapour pressure of pyridinium chloride at 160°C, the temperature at which most of the experiments were carried out, necessitated sealing the spectrophotometer cells to prevent solvent loss from evaporation during an experiment.

The optical cells used for this work were 1 cm Pyrex cells to which a circular tube was attached. This tube was sealed off under helium after the cells had been filled with salt.

After a run, chemical analyses for uranium were performed by opening the tube and dissolving weighed portions of the salt in water.

The density of pyridinium chloride was determined to be 1·142 g/cm³ at 160°C. Using this value and the analytical results on uranium, molar extinction coefficients were calculated.

C. $LiNO_3$–KNO_3 *eutectic*. $LiNO_3$–KNO_3 eutectic (about 43 mol % $LiNO_3$, m.p. about 132°C) was prepared by fusing reagent grade chemicals in the proper proportions. The melts were dehydrated by bubbling dry N_2 through them for 1 hr. Dissolution of anhydrous uranium compounds in melts prepared in this way results in clear solutions. Ordinary Beckman 1 cm Pyrex cells were used for this work. No special precautions had to be taken to exclude moisture when working with these fused salt solutions. After an experiment, the contents of a cell were transferred to a weighing bottle and weighed portions of the solidified material analysed for uranium. Densities of $LiNO_3$–KNO_3 eutectic were determined at a number of temperatures. At 160°C for example, the density was found to be 1·942 g/cm³. From the measured density values and the chemical analyses, molar extinction coefficients were calculated.

Uranium salts. Uranium tetrafluoride was furnished by the Metallurgy Division of ANL. Spectroscopic analysis of this material showed the impurity concentrations to be in the p.p.m. range. Chemical analysis gave an oxygen content of less than 0·1 wt. per cent.

Uranium tetrachloride, UCl_4, was prepared by refluxing UO_3 with hexachloropropylene. The excess hexachloropropylene was distilled off at the conclusion of the reaction and the crude reaction

[9] E. R. VAN ARTSDALEN and I. S. YAFFEE, *J. Amer. Chem. Soc.* **59**, 118 (1955).

product was sublimed in a vacuum. Both the UO_3 starting material and the UCl_4 product were analysed chemically. The product was at least 99·8 % UCl_4.

Anhydrous uranyl chloride, UO_2Cl_2, was prepared by treating UCl_3 with O_2 gas at 350°C. Chemical analysis for U and Cl showed it to be at least 99·5 % UO_2Cl_2. The sample was kindly furnished by Dr. H. R. HOEKSTRA of the Chemistry Division.

Dicesium uranium hexachloride, Cs_2UCl_6, was prepared by slow evaporation over P_2O_5 of aqueous hydrochloric acid solutions of U(IV) and CsCl. These solutions were prepared by dissolving reagent grade CsCl and UCl_4 in O_2 and CO_2 free water. Crystals of Cs_2UCl_6 grew in flat hexagonal plates in a vacuum desiccator filled with N_2 to a pressure of 0·3 atm. The compound was analysed gravimetrically for U and Cl and found to be at least 99·8% Cs_2UCl_6.

DISCUSSION AND RESULTS

In general each oxidation state of a metal ion has a characteristic absorption spectrum which may become modified to some extent by complex ion formation. The spectrophotometric method has been extensively used to study oxidation states and complex ions in aqueous solutions and in crystals. It has recently been shown[2,3] that the absorption spectra of many transition metal ions in fused salts and the changes occurring in these spectra when complex ions are formed may be correlated closely with the absorption spectra of these ions in aqueous solutions and in crystals.

The oxidation states of a metal ion that can be observed in a given solution are limited by the oxidation–reduction potential of the solvent. In water the stable oxidation states are limited to a range of about 1·2 V exclusive of overvoltages.[10] The ionic species existing in a given solution on the other hand will be determined by the co-ordination properties of the solvent. Thus in water, metal ions in the absence of competing ligands will be co-ordinated to the oxygen atoms of the water dipoles.

Very little is known regarding either the oxidation–reduction or the complex-forming properties of fused salts. Consequently it is difficult to predict what oxidation states or complex ions can exist in these solvents. To obtain information of this sort for uranium solutions, the fused salts LiCl–KCl eutectic, pyridinium chloride and $LiNO_3$–KNO_3 eutectic were studied. These solvents could be expected to differ markedly in their oxidation-reduction as well as their complex-forming behaviour and could provide information from which to predict the properties of uranium in some other fused salt solvents.

A. *Solutions in* LiCl–KCl *eutectic*

The range of oxidation-reduction potential spanned by the LiCl–KCl eutectic is about 3·5 V exclusive of overvoltages.[11,12] It is of interest therefore to explore oxidation states in this solvent, particularly since oxidation states that are unstable in water might be capable of existence in this medium.

To prepare solutions in a known oxidation state, uranium tetrafluoride was dissolved in LiCl–KCl to give green solutions of U(IV). These solutions are exceedingly sensitive to traces of water with which the U(IV) reacts to form dark coloured precipitates. The precipitates are almost certainly uranium oxides but their composition has not yet been determined. The U(IV) solutions react only slowly with dry oxygen gas to give yellow solutions of U(VI). Very rapid oxidation to the U(VI) state occurs however on addition to the U(IV) solutions of solid anhydrous nitrates like KNO_3.

[10] W. M. LATIMER, *Oxidation Potentials* (2nd Ed.) Prentice-Hall, New York (1952).
[11] Y. K. DELIMARSKII, *Zh. Fiz. Khim.* **29**, 28 (1955).
[12] H. A. LAITINEN and C. H. LIU, *J. Amer. Chem. Soc.* **80**, 1015 (1958).

Yellow solutions of U(VI) were also prepared by dissolution of UO_2Cl_2 in LiCl–KCl eutectic.

In order to produce lower oxidation states of uranium, metals were used as reductants. Spectroscopically pure Al or U wire reduce U(IV) solutions to U(III), resulting in a dramatic colour change from green to red. It was found convenient to carry out these reductions by placing a strip of Al or U wire in the bottom of the optical cell and retaining it there during the optical measurements. In the case of Al, care had to be taken to pump off all HCl dissolved in the eutectic prior to sealing off the cell otherwise

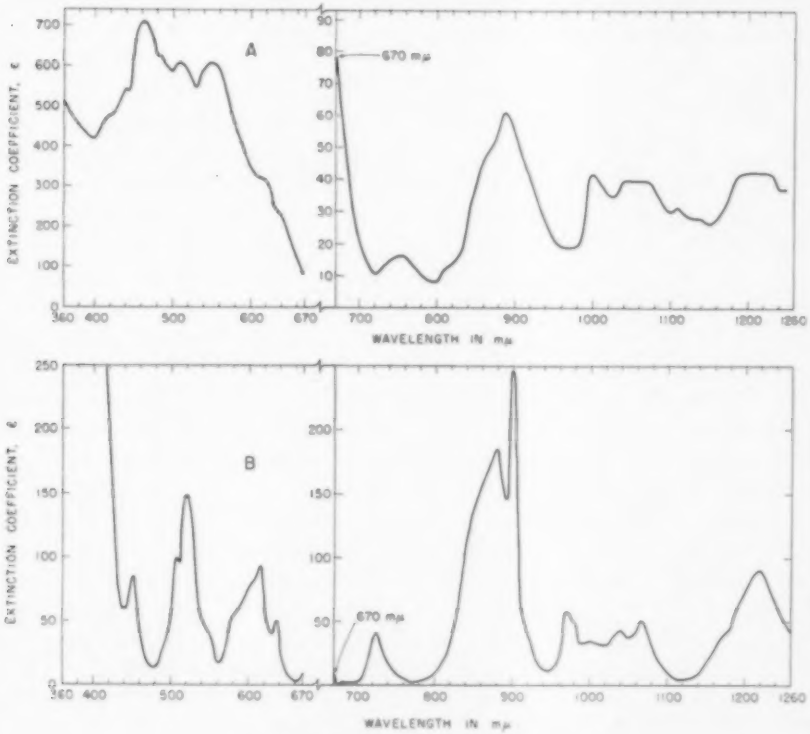

FIG. 3.—Absorption spectra of U(III).
Curve *A*: LiCl–KCl eutectic at 400°C
Curve *B*: 1 M $HClO_4$ at 25°C.

reaction with the Al occurred leading to the formation of H_2 gas bubbles which interferred with the optical measurements. This difficulty was not nearly as pronounced when U metal was used as reductant. Under these conditions the rate of reaction of HCl appears to be much slower with U than with Al. U(III) solutions in LiCl–KCl eutectic were found to be even more sensitive to oxidation by traces of O_2 or H_2O than U(IV) solutions.

Reduction to U metal occurred when Mg metal was placed in contact with U(IV) solutions. Uranium metal precipitated from solution as finely divided particles and also as a black coating on the surface of unreacted Mg metal.

An electromotive force series of metals in the LiCl–KCl eutectic has recently been established by the work of LAITINEN and LIU.[12] Their measurements were made

relative to a 1 M Pt(II)-Pt(0) electrode which was taken to have an $E^\circ = 0{\cdot}000$. On the basis of the metal reduction experiments described above the U(IV)–U(III) potential can be expected to be more positive than $-1{\cdot}77$ V and the U(III)–U(0) potential to lie between $-1{\cdot}77$ V and $-2{\cdot}58$ V in the LiCl–KCl eutectic.*

Uranium(III) *spectrum.* The U(III) spectrum (Fig. 3A) in the LiCl–KCl eutectic at 400°C is characterized by a number of absorption bands spread over the entire spectral region, 360 mμ to 1260 mμ, in which measurements were made. For comparison with an aqueous solution spectrum, the data of STEWART[13] on a U(III) solution in 1 M $HClO_4$ is also given. (Fig. 3B). The correlation between the number and wavelengths of the absorption bands of the two spectra is good, particularly at wavelengths longer than 700 mμ.

In this long wavelength region of the spectrum, the molar extinction coefficients of the bands in aqueous solution are three to four times as large as the analogous bands in the fused salt. However, since the bands in the latter solvent are in general somewhat broader than in the former, transition probabilities in the two media cannot be compared until calculations of oscillator strengths have been carried out for the fused salt solutions.

At about 700 mμ, an intense and complex absorption band begins which reaches molar extinction coefficients of 600–700 in the 600 mμ–500 mμ region. The absorption curve then falls again, reaching a minimum at 400 mμ only to rise once more at still lower wavelengths. The rapid rise in light absorption at about 700 mμ is primarily responsible for the red colour of the solution. In this region of the spectrum the extinction coefficients are larger by a factor of three or four in the fused salt compared with the aqueous perchloric acid solutions, just the reverse of the situation at longer wavelengths.

It is a well known fact that the colour of U(III) solutions in aqueous HCl solutions becomes very much intensified with increasing HCl concentrations.[14] Indeed, U(III) solutions in concentrated HCl are red. These colour changes have recently been studied spectrophotometrically by JORGENSEN,[15] who found a shift of the 521 mμ band to 540 mμ and its intensification by a factor of about five with increasing HCl concentration. There can be little doubt that the spectral changes in aqueous solutions are associated with the formation of chlorocomplexes of U(III).[15,16] In the LiCl–KCl fused salt solution, U(III) finds itself in a pure chloride ion environment. The intense band between 500 mμ and 600 mμ (by analogy with the conc. HCl solution spectrum) may be taken as evidence for the existence of U(III) chlorocomplexes in the melt. The detailed nature of these complexes has not yet been elucidated but it is hoped that future studies of U(III) spectra in crystals will shed light on this point.

Uranium (IV) *spectrum.* The U(IV) spectrum taken at 400°C is shown in Fig. 4A. For comparison, the U(IV) spectrum in 1 M $HClO_4$ at 25° is shown in Fig. 4B. It can be seen that certain features of the spectra are not much altered despite the drastic change in solvent and temperature. For example, prominent absorption bands occur in the 600–700 mμ and the 1000–1200 mμ regions in both solvents. The extinction

* We have recently measured the U(III)–U(0) potential in LiCl–KCl eutectic and find an $E^\circ = -2{\cdot}34$ V vs. a IM Pt. electrode. This work was done in collaboration with Dr. ROBERT OSTERYOUNG of of Rensselaer Polytechnic Institute, Troy, New York.

[13] D. C. STEWART, *Absorption Spectra of Actinide and Lanthanide Rare Earths*, *ANL*-4812, Unclassified (1952).
[14] K. SOMEYA, *Z. Anorg. Chem.* **161,** 46 (1927).
[15] C. K. JØRGENSEN, *Acta Chem. Scand.* **10,** 1503 (1956).
[16] R. M. DIAMOND, K. STREET and G. T. SEABORG, *J. Amer. Chem. Soc.* **76,** 1461 (1954).

coefficients of the bands are smaller by a factor of about four in the fused salt as compared with aqueous solution; however, no comparison of absolute absorption intensities has been made as yet. At wavelengths shorter than 600 mμ, very pronounced differences are found in comparing the fused salt with the aqueous solution spectra. For example, in the fused salt an intense absorption band starts at 400 mμ which in

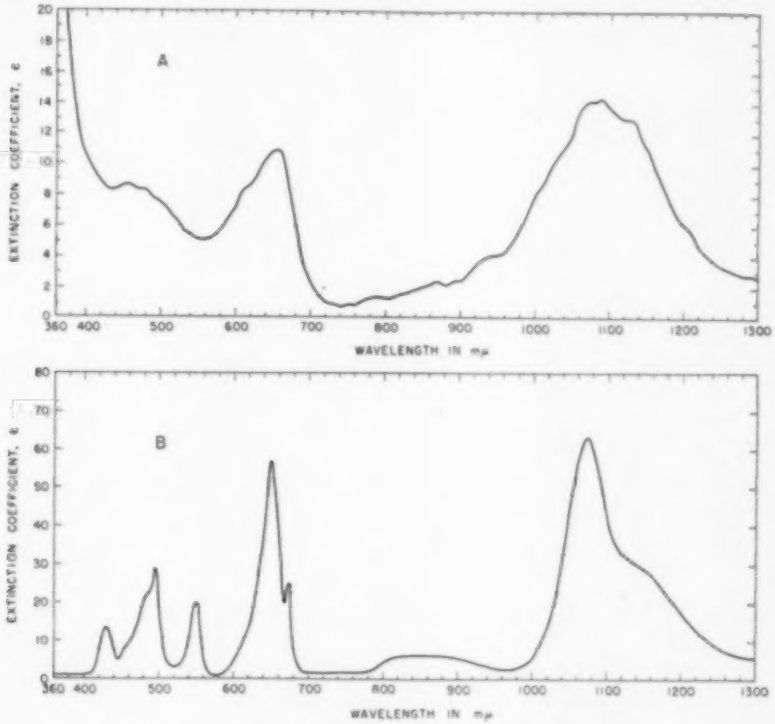

FIG. 4.—Absorption spectra of U(IV).
Curve *A*: LiCl–KCl eutectic at 400°C
Curve *B*: 1 M $HClO_4$ at 25°C.

all probability is a charge transfer band. In perchloric acid solutions of U(IV) there is virtually no absorption in the region 400–225 mμ. Only at wavelengths below 225 mμ does one observe the intense absorption of a charge-transfer band. The occurrence of a charge-transfer band at lower energies in the chloride eutectic as compared with perchloric acid solutions is not unreasonable since the energy required to transfer an electron from a chloride in to a U(IV) ion is probably less than for a similar process involving a water molecule and a U(IV) ion.

It is of interest to see what can be learned from the spectra about the chloride ion environment of the U(IV) ions in the melt. If one assumes that in aqueous solution U(IV) exists as an octahydrated species, the similarity of the U(IV) spectra in LiCl–KCl eutectic and in perchloric acid solution would suggest that the co-ordination number is eight in the eutectic melt as well. Uranium (IV) can exhibit a co-ordination number of eight for chloride ions in the solid state as in the compound UCl_4,[17] and so

[17] R. C. L. MOONEY, *Acta Cryst.* **2**, 189 (1949). In crystalline UCl_4, each U(IV) ion is surrounded by eight chloride ions, four at a distance of 2·5 Å and the remaining four at a distance of 3 Å.

it is not unreasonable to suppose that the same co-ordination number can occur in some chloride melts.

However, in other compounds such as Cs_2UCl_6 and $[(CH_3)_4N]_2UCl_6$, U(IV) has a co-ordination number of six.[18,19,20] The absorption spectra of these two crystals taken at room temperature on a Cary spectrophotometer are reproduced in Fig. 5A. To within the resolving power of the instrument, the spectra of the two crystals are identical. The great similarity of these spectra is due to the fact that in both crystals

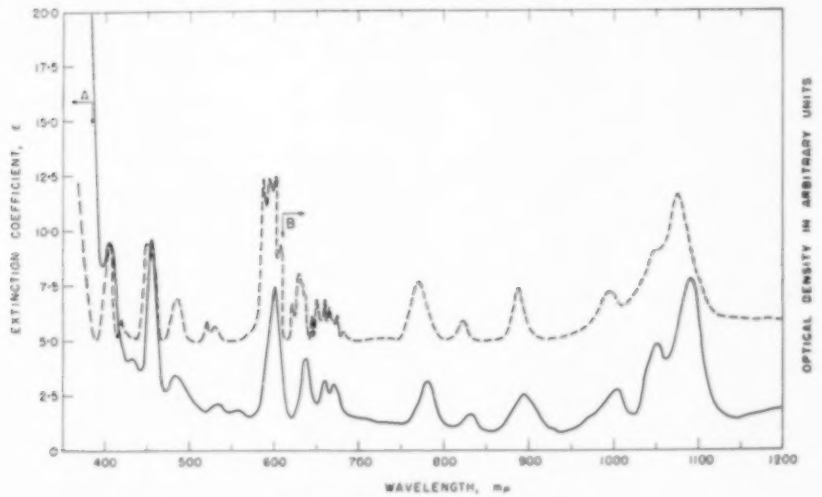

FIG. 5.—Absorption spectra of U(IV).
Curve *A*: Single crystals of $[(CH_3)_4N]_2UCl_6$ and Cs_2UCl_6 at R.T.
Curve *B*: Solution in fused pyridinium chloride at 160°C

U(IV) is surrounded octahedrally by six chloride ions. In a survey of absorption spectra of transition metal ions in fused pyridinium chloride (m.p. 144°C), we had occasion to examine the spectrum of UCl_4 dissolved in this melt. (See Fig. 5B.) It can be seen that this spectrum matches the crystal spectra very closely, the absence of fine structure in some of the bands of the melt spectrum being due primarily to the higher temperature. On the basis of these results, it is tempting to suggest that in the pyridinium chloride melt, each U(IV) ion is octahedrally surrounded by six chloride ions. A theoretical study of the absorption spectra at low temperatures of crystals of Cs_2UCl_6 and $[(CH_3)_4N]_2UCl_6$ has resulted in the identification of certain structural features of these spectra with vibrational-electronic transitions.* For example, the three bands in the 1000–1100 mμ region are thought to arise from transitions between various vibrational levels of the ground state of a $UCl_6^{=}$ molecular ion to vibrational levels of an excited electronic state. If this interpretation is correct, certain interesting conclusions can be drawn concerning the ionic species in the melt, since the spectral features due to the vibrational-electronic transitions in the crystals appear to be so largely preserved in the melt. Vibrational-electronic transitions can occur and hence

* The detailed results of this study, which is being carried out in collaboration with PROFESSOR R. SATTEN of the University of California at Los Angeles, will be published in full elsewhere.

[18] W. H. ZACHARIASEN, *Acta Cryst.* **1**, 268 (1948).
[19] S. SIEGEL, *Acta Cryst.* **9**, 827 (1956).
[20] E. STARITZKY and J. SINGER, *Acta Cryst.* **5**, 536 (1952).

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can be observed only if the $UCl_6^{=}$ species in the melt has a lifetime comparable to the time required for the transition. The time for a vibrational-electronic transition is typically of the order of 10^{-9} sec. Thus, a lower limit is set on the lifetime of the $UCl_6^{=}$ complex ion in the melt.

There is as yet no satisfactory explanation for the change from eight fold to six fold co-ordination of U(IV) in going from the LiCl–KCl eutectic to pyridinium chloride as a solvent.

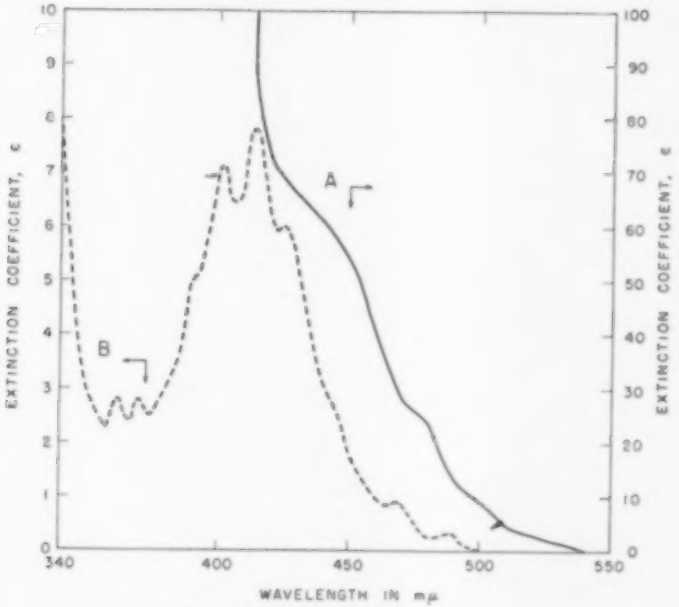

FIG. 6.—Absorption spectra of UO_2(II).
Curve *A*: LiCl–KCl eutectic at 400°C
Curve *B*: 1 M $HClO_4$ at 25°C.

UO_2(II) *spectrum.* Identical spectra of UO_2(II) were obtained in LiCl–KCl eutectic by dissolving either anhydrous UO_2Cl_2 or oxidizing a U(IV) solution with KNO_3. The spectrum of the yellow solutions is shown in Fig. 6A. Immediately below it is shown the familiar spectrum of uranyl ion in 1 M perchloric acid (Fig. 6B).

In aqueous solutions and in crystals of uranyl compounds, the band with maximum at $\approx$425 mμ is due to an electronic transition within the uranyl ion while the fine structure of the band is due to vibrational energy levels superimposed on the electronic transition. In perchloric acid solution the charge transfer band begins at about 350 mμ and so is well separated from the intramolecular electronic transition of the uranyl ion.

In the LiCl–KCl melt, however, the charge transfer band appears to be shifted to considerably lower energies while the intramolecular electronic transition occurs at about the same energy as in aqueous solution. As a result, the uranyl absorption band overlaps the intense charge-transfer band and appears merely as a shoulder on the long wavelength side of the charge-transfer band. The vibrational fine structure has almost completely disappeared in the eutectic solvent. The existence of the uranyl species in

these melts is further evidence of the remarkable stability of the $(O–U–O)^{2+}$ molecular grouping. Attempts were made to oxidize U(IV) solutions to U(V) or U(VI) in the absence of O_2 by bubbling Cl_2 through the melt. No changes in the U(IV) spectrum of the initial solution were observed even after prolonged treatment with Cl_2 indicating that the non-oxygenated higher oxidation states of uranium are unstable under these conditions.

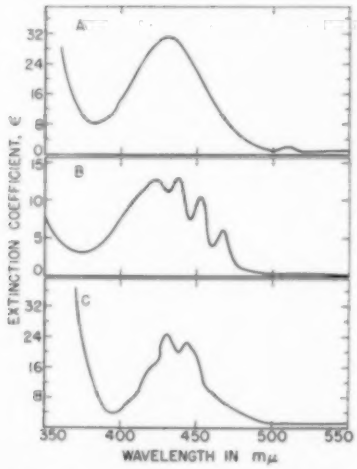

FIG. 7.—Absorption spectra of UO_2(II).
Curve *A*: $LiNO_3$–KNO_3 eutectic at 160°C
Curve *B*: 10 M HNO_3 at 25°C
Curve *C*: $LiNO_3$–NH_4NO_3–NH_4Cl eutectic at 160°C.

B. *Solutions in* $LiNO_3$–KNO_3 *eutectic*

The experiments described above show that the LiCl–KCl eutectic served as an inert solvent in carrying out oxidation–reduction reactions on uranium. It was to be expected that nitrate melts on the other hand would exhibit oxidizing was well as acid base properties in the presence of uranium. When UCl_4 was added to $LiNO_3$–KNO_3 eutectic at a temperature of about 175°C brown fumes were given off. The resultant solution was yellow. Presumably the reaction giving rise to these products was

$$U^{4+} + 2NO_3^- = UO^{2+} + 2NO_2 \quad (1)$$

The uranyl ion solution was stable up to a temperature of about 300°C, when a yellow precipitate was formed. Although the nature of this precipitate has not yet been established, it is almost certainly either UO_3 or an alkali metal uranate or diuranate. Formally, this reaction may be written:

$$UO_2^{2+} + 2NO_3^- = UO_3 + 2NO_2 + \tfrac{1}{2}O_2 \quad (2)$$

Reaction (2) is an acid–base reaction which may be thought of as proceeding in the following way

$$NO_3^- = NO_2^+ + O^{2-} \quad (3)$$

$$NO_2^+ + NO_3^- = 2NO_2 + \tfrac{1}{2}O_2 \quad (4)$$

According to this formalism, the oxide ion released in reaction (3) reacts with UO_2^{2+} to form UO_3. An analogous set of reactions may be written if the products are alkali metal uranates or diuranates.

Dissolution of anhydrous UO_2Cl_2 in the $LiNO_3$–KNO_3 eutectic proceeded smoothly to give a yellow solution.

A typical spectrum of one of the solutions of UO_2(II) in $LiNO_3$–KNO_3 eutectic is shown in Fig. 7A. Except for the continuum in the ultra-violet, the spectrum consists of a single smooth band with maximum at 430 mμ and a molar extinction coefficient equal to thirty-one. This band may be compared with the analogous transition of uranyl ion in 10 M HNO_3 shown in Fig. 7B. It will be noted that the extinction coefficients in the melt are approximately twice as large as in 10 M HNO_3 indicating that a mechanism is operative in the melt to relax somewhat the forbiddenness of this electronic transition. In addition, the melt spectrum gives no indication of vibrational fine structure. The lack of structure and greater intensity of the melt spectrum is reminiscent of the featureless but quite intense absorption band of UO_2(II) in water solutions of pH > 4. In solution of high pH, UO_2(II) is appreciably hydrolysed.[21] It is possible that the additional U–O bands which are formed in hydrolysed aqueous uranyl solutions introduce new molecular vibrations which tend to smear out the vibrational fine structure of the uranyl group itself. Similarly, in the nitrate melt, the co-ordination of U to nitrate oxygens could result in many new U–O frequencies which make it impossible to resolve the vibrational fine structure. It is interesting to note that the uranyl ion spectrum in the ternary eutectic NH_4NO_3–$LiNO_3$–NH_4Cl (Fig. 7C) does show some vibrational fine structure. In the presence of chloride ion, chloro-complexes of UO_2(II) are formed in the nitrate melt, as has previously been shown by the elution behaviour UO_2(II) from γ–Al_2O_3 columns.[3] The formation of chloro-complexes proceeding by the replacement of nitrate groups in the uranium coordination sphere with consequent breaking of U–O bands could be the mechanism responsible for the re-emergence of vibrational fine structure in the uranyl absorption band.

Acknowledgements—It is a pleasure to acknowledge the help of Mr. K. JENSEN, who performed the uranium analyses.

[21] S. AHRLAND, *Acta Chem. Scand.* **3**, 374 (1949).

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THE PROPERTIES OF INORGANIC COMPOUNDS IN ORGANIC SOLVENTS—II

THE ION EXCHANGE REACTIONS OF QUADRIVALENT PLUTONIUM IN DIETHYLENE GLYCOL DIBUTYL ETHER

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Abstract—The ion exchange reactions of plutonium(IV) nitrate extracted into diethylene glycol dibutyl ether (butex) from aqueous nitric acid have been investigated. For both cation and anion resins considerable sorption of plutonium occurred; in both systems, maximum values of K_d were found at nitric acid concentrations in the solvent of about 0·4 M. The effect of nitric acid on the distribution coefficients has been correlated with the plutonium species present; in strong nitric acid plutonium(IV) appears to exist as solvated $H_2Pu(NO_3)_6$, $Pu(NO_3)_4$ having little stability in this solvent. The ion exchange behaviour has also been studied in solutions of perchloric acid in butex.

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DESPITE the increasing application of ion exchange resins in analytical and physical chemistry, there have been relatively few attempts to investigate their behaviour in non-aqueous solvents. CHANCE *et al.*[1] have discussed the literature up to 1953; practically all the work reviewed by them, and that published since, has been with hydrophilic solvents and substances easily soluble in such solvents. KATZIN and GEBERT,[2] for example, investigated the reaction of cobalt and nickel nitrates and lithium chloride dissolved in acetone with anion exchange resin. It was found that molecular species were absorbed by the resin, with no true ion exchange occurring. The present work is concerned with the ion exchange reactions of species which can pass into organic solution only as the result of solvent extraction from the appropriate aqueous phase (which is subsequently removed). In this field, an anion exchange separation has been used by one of us in the study of the chloride exchange between hydrochloric and chloroauric acids extracted into $\beta\beta'$-dichlorodiethyl ether.[3] Organic solutions of this type offer an interesting field for the investigation of inorganic species existing in, and extracted into, non-aqueous media.

The present investigation began with attempts to use short ion exchange columns to remove plutonium from organic solutions. The results suggested the need for an investigation of the species present, and the correlation of the nature of these species with the distribution ratios found in a series of equilibrium experiments.

EXPERIMENTAL

Materials. Stock aqueous solutions of plutonium(IV) nitrate were prepared by the method given in an earlier paper.[4] Nitric and perchloric acids were A.R. grade materials, butex (diethylene glycol dibutyl ether) was as previously described.[5]

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[1] F. S. CHANCE, G. E. BOYD and H. J. GARBER, *Industr. Engng. Chem.* **45**, 1671 (1953).
[2] L. I. KATZIN and E. GEBERT, *J. Amer. Chem. Soc.* **75**, 801 (1953).
[3] D. G. TUCK, C. D. CORYELL and J. W. IRVINE, *J. Phys. Chem.* **60**, 577 (1956).
[4] D. G. TUCK, *J. Inorg. Nucl. Chem.* **6**, 252 (1958).
[5] D. G. TUCK, *J. Chem. Soc.* 3202 (1957).

The preparation of solutions of nitric and perchloric acids in butex was discussed in the preceding paper, as was the preparation and analysis of plutonium (IV) solutions in butex containing nitric acid.

Two ion exchange resins were used in this work: Amberlite IRA-400, a strongly basic anion exchanger and Amberlite IR-120, a polystyrene sulphonic acid cation exchanger. Both were analytical grade materials, supplied by Messrs. B.D.H. Ltd. Amberlite IRA-400, received in the hydroxide form, was converted to the nitrate in bulk, thoroughly washed, taken back to the hydroxide form and finally reconverted to the nitrate. The product was washed to remove "fines" and dried overnight at 60°C; this temperature was used to minimize reaction of the resin with any occluded nitric acid. The dry resin was sieved and the fraction (>BS 85, <BS 22) stored in a stoppered bottle to prevent absorption of moisture. Amberlite IR-120 supplied as the hydrogen ion form, was converted to the sodium form and then back to the hydrogen form, followed by washing drying and sieving. Both resins were also used in other forms in certain experiments; in such cases, the preparative procedure was similar to that just described.

Determination of distribution coefficients. In each experiment, a weighed quantity of resin was added to 5 ml of butex, of pre-determined acidity, contained in a stoppered tube; the amount of the resin was normally 50 mg or less. The mixture was allowed to stand for about 30 min for the resin to come to equilibrium with the solution. A small aliquot (100 μl) of a standard solution of plutonium (IV) in butex ($\sim 5 \times 10^7$ dpm/ml) was added, the stopper of the tube bound in position with linen tape and the tube shaken mechanically for about 5 hr. The resin was then allowed to settle out, and aliquots (50 μl) were withdrawn for evaporation on stainless steel trays[6] for α-counting. Care was taken that no particles of resin were drawn into the micropipette used for sampling. In some cases, larger aliquots (1 ml) were titrated with aqueous caustic soda to check that no acidity change had occurred during the agitation. All experiments were carried out at room temperature ($\sim$21°C). The results of these experiments give equilibrium distribution coefficients of plutonium (IV) between resin and solution phases.

RESULTS

Exchange with Amberlite IRA-400 (NO_3^-). With this resin, the effect of variations in nitric acid concentration on the distribution was investigated. The distribution coefficient is defined as

$$K_d = \frac{\text{concentration of Pu on resin (dpm/g)}}{\text{concentration of Pu is solution(dpm/ml)}}$$

The results of these experiments are shown in Fig. 1. The wide range of K_d values is remarkable, as is the well-defined maximum at approximately 0·4 M nitric acid. In a subsequent experiment, resin which had been quickly dried at room temperature was compared with that dried at 60°C; no significant difference in behaviour was detected. CHANCE *et al.*[1] suggest that wet resin is more efficient than dry material in removing sodium bromide from organic solutions. The solutions used in the present work, however, were prepared by solvent extraction of aqueous solutions, so that the nitric acid at least was hydrated[5,7]; it is therefore perhaps not surprising that no change in distribution was observed. This point is discussed below.

Exchange with IR-120 (H^+). The effects of changes of nitric acid concentration on distribution coefficient have been investigated with this resin also, giving the results shown in Fig. 2. This series of experiments was not extended to high nitric acid concentrations since the difficulties involved in the preparation of samples for α-counting in the presence of excess nitric acid render the measurement of the very low K_d values quite unreliable. A maximum K_d is again found at $\sim$0·4 M nitric acid, although the values of K_d in this system are higher than for anion exchange by a factor of about 10 at the same acidity.

[6] D. G. TUCK, *Anal. Chim. Acta* **17**, 271 (1957).
[7] H. A. C. MCKAY, *J. Inorg. Nucl. Chem.* **4**, 375 (1957).

Exchange with IR-120 (H^+) *and IRA*-400 (ClO_3^-). The behaviour of plutonium (IV) in aqueous perchloric acid is significantly different from that in nitric acid. Accordingly, we have measured the distribution coefficient of plutonium between the ion exchange resins and solutions of perchloric acid in butex. The method was essentially the same as that described above. It should be noted, however, that the final solution contained small amounts of nitric acid from the aliquot of plutonium (IV) stock solution; the final nitric acid concentration was approximately 0·05 M.

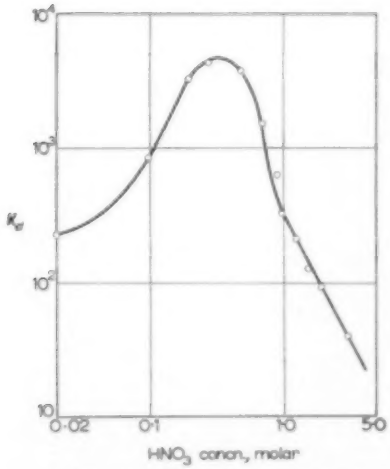

Fig. 1.—Distribution of Pu(IV) between IRA-400 (NO_3^-) and butex at varying HNO_3 concentrations.

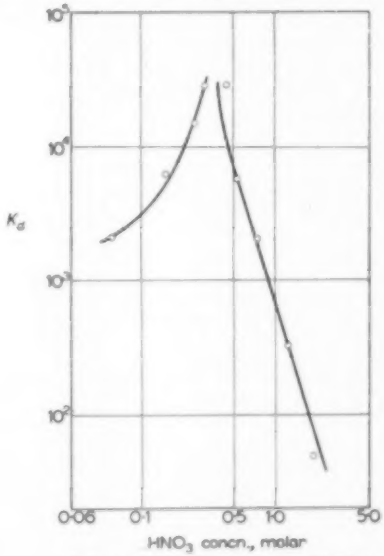

Fig. 2.—Distribution of Pu(IV) between IR-120 (H^+) and butex at varying HNO_3 concentrations.

For the cation exchanger IR-120 (H^+), the take-up of plutonium on to the resin is high, and varies with perchloric acid concentration in the manner shown in Fig. 3. For the anion exchanger in the perchlorate form, the K_d values are low and increase slightly with decreasing perchloric acid concentration.

Table 1.—Distribution of Pu(IV) between IRA-400 (ClO_4^-) and butex at varying $HClO_4$ concentrations

$HClO_4$ concn. (M)	0·27	0·81	1·35	1·79
K_d	14·0	6·5	6·0	5·2

Absorption spectrum of plutonium(IV) *in butex*. The absorption spectrum of plutonium(IV) in weak nitric acid solutions in butex has been discussed previously.[4] In strong nitric acid, the solution obtained by solvent extraction of plutonium(IV) nitrate from 10 M aqueous nitric acid is pale green in colour, and apparently quite stable over the period of examination (three months). The absorption spectrum of such a solution, 3·3 M in nitric acid, is shown in Fig. 4.

Precipitation on to ion exchange resins. Experiments were carried out to investigate the possibility of using ion exchange resins to remove plutonium from organic solution by the precipitation technique.[8] Lithium, sodium and potassium forms of IR-120 were used, but the take-up of plutonium was low for all three forms of the resin.

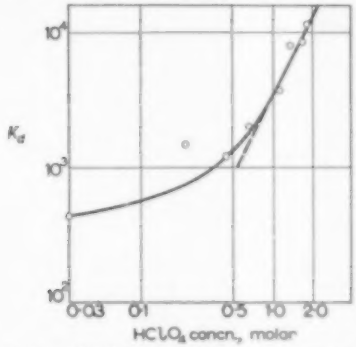

FIG. 3.—Distribution of Pu(IV) between IR-120 (H^+) and butex at varying $HClO_4$ concentrations.

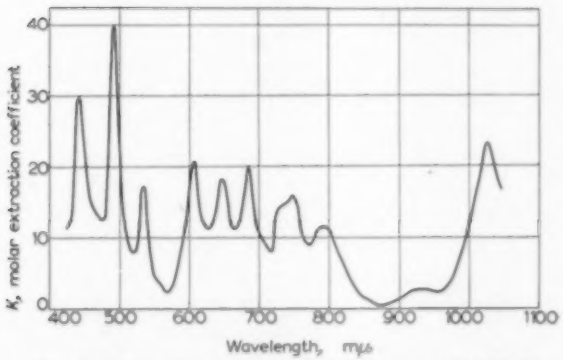

FIG. 4.—Absorption spectra of Pu(IV) in butex 3·3 M HNO_3.

DISCUSSION

Plutonium(IV) *species in butex*

The colour changes observed on diluting a solution of plutonium(IV) in butex have been discussed previously.[4] The spectrum of the species present in strong nitric acid solutions in this solvent closely resembles that given by HINDMAN[9] for plutonium(IV) in 11 M aqueous nitric acid; Table 2 shows that the ratio of the molar extinction coefficients for five of the eight peaks is sensibly constant.

Of the absorption maxima for which the ratio given in the last column of Table 2 is significantly different from 1·15, that at 491 mμ is known to be critically dependent upon nitric acid concentration both with respect to wavelength and to molar extinction coefficient. There appears to be little influence due to solvent interaction in the spectrum in butex, the only major difference from the aqueous spectrum being that

[8] R. H. JAMES and G. A. WELCH, *Nature, Lond.* **177**, 183 (1956).
[9] J. C. HINDMAN, *The Actinide Elements* NNES, Plutonium Project Record, Div. IV, Vol. 14 A, McGraw-Hill, p. 340. New York (1954).

TABLE 2.—SPECTRAL MAXIMA FOR Pu(IV) IN STRONG NITRIC ACID

aq. 11 M HNO_3		3·3 M HNO_3 in butex		κ_{max} for 11 M HNO_3 (aq) / κ_{max} for 3·3 M HNO_3 (butex)
Wavelength (mμ)	κ_{max}	Wavelength (mμ)	κ_{max}	
443	35·8	443	30·2	1·18
491	51·6	492	40·2	1·28
535	19·7	535	17·4	1·13
608	23·9	608	20·8	1·15
648	20·6	646	18·3	1·13
683	19·4	681	19·2	1·01
742	21·7	746	16·0	1·35
795	13·3	794	11·5	1·16

the peak at 742 mμ has a "shoulder" on the low wavelength side, for which there is no analogy in the aqueous system. This may be connected with the divergence in the ratio $\kappa_{max}^{(aq)}/\kappa_{max}^{(butex)}$ for the absorption maxima at 683 and 746 mμ.

In 11 M aqueous nitric acid the main species[9] is $Pu(NO_3)_6^{2-}$ or $H_2Pu(NO_3)_6$. It is most unlikely that the species which passes across the liquid–liquid interface during extraction, or which exists in a low dielectric constant medium such as butex, is the charged ion. For the extraction of the transition elements, there seems to be little doubt that the relevant species is the neutral acid HMX_4, corresponding to the ion MX_4^-.[10,11,12] The absorption spectra of organic and aqueous solutions of such species are almost identical[13,14]; Raman spectroscopy shows that in at least one case[15] the molecules exist as the associated ion-pair $(H^+)(MX_4^-)$. On this basis, together with the strong similarities already noted in the spectra, we shall assume that in strong nitric acid solutions in butex, plutonium(IV) is present as $H_2Pu(NO_3)_6$. This species is almost certainly solvated by one or more butex molecules; KEMP *et al.*[16] have, in fact, isolated a crystalline complex of plutonium hexanitrate, water and butex. Evidence presented previously[4] suggests that on lowering the nitric acid concentration, the hexanitrato acid dissociates to give $Pu(NO_3)_4$ which is unstable to hydrolysis. The instability of this species in butex is in marked contrast to its behaviour in tri-*n*-butyl phosphate.[17] These differences presumably arise mainly from the differing interaction of $Pu(NO_3)_4$ with the two solvents; steric reasons may prevent the formation of an "inner complex" with butex, whereas there seems to be good evidence that in tri-*n*-butyl phosphate plutonium(IV) is fully co-ordinated as $Pu(NO_3)_4$ 2TBP. Apart from the effect on the stability of the tetranitrato complex, however, it does not seem necessary to consider "solvation" in discussing the results of the ion exchange experiments.

[10] J. AXELROD and E. H. SWIFT, *J. Amer. Chem. Soc.* **62**, 33 (1940).
[11] N. H. NACHTRIEB and R. E. FRYXELL, *J. Amer. Chem. Soc.* **71**, 4035 (1949).
[12] H. IRVING and F. J. C. ROSSOTTI, *J. Chem. Soc.* 1927, 1938, 1946 (1955).
[13] H. L. FRIEDMAN, *J. Amer. Chem. Soc.* **74**, 5 (1952).
[14] H. M. NEUMANN, *J. Amer. Chem. Soc.* **76**, 2611 (1954).
[15] L. A. WOODWARD and P. T. BILL, *J. Chem. Soc.* 1699 (1955).
[16] E. F. KEMP, D. A. CHARMAN and N. JACKSON. Unpublished data (1950).
[17] G. F. BEST, H. A. C. MCKAY and P. R. WOODGATE, *J. Inorg. Nucl. Chem.* **4**, 315 (1957).

As noted above, it can be assumed that in a weakly basic solvent of low dielectric constant, polar molecules will be almost completely undissociated. In this way no distinction is made between un-ionized molecules like HNO_3 and associated ion-pairs, such as $(H^+)(NO_3^-)$; free ions will only be present in negligible concentrations, but of course inter-ionic reactions (such as ion exchange) can occur through ion-pair interactions. This makes possible the further assumption that activities can be equated with concentrations since the inter-ionic attraction effects will be much less than in aqueous solution. There is, in any case, some evidence from the mass-action data on the extraction of nitric acid into butex[5] that the activity of nitric acid in this solvent is proportional to the concentration over the range studied. For plutonium the concentration is so low throughout that under any given conditions activity is proportional to plutonium concentration.

Compared with normal ion exchange work, our experiments were carried out at very low water concentrations. However, because of the solubility of water in butex (about 1·4 per cent) and the presence of water carried into the solvent by the acid, there was always a reasonable excess of water present over that required for the very small amount of resin to reach equilibrium. Furthermore, in an experiment using "wet" resin there was no significant difference in exchange due to the water content of the resin. It is therefore reasonable to assume that distribution ratios were not dependent upon the water content of the resin, particularly at the higher concentrations at which attempts are made to identify the species present.

The ion exchange resins used were strong acid and strong base resins containing only one functional group each. It will therefore be assumed that the uptake of plutonium is proportional to the concentration of the exchanging plutonium species in the solvent, as long as only trace amounts of plutonium are present, other conditions being constant.

Ion exchange between Pu(IV) *and IRA*-400(NO_3^-) *in nitric acid solutions in butex*

In strong acid the plutonium species is assumed to be $H_2Pu(NO_3)_6$; the reaction of this species with the resin can be written in the following manner:

$$H_2Pu(NO_3)_6 + 2RNO_3 \overset{K_1}{\rightleftharpoons} R_2Pu(NO_3)_6 + HNO_3 \qquad (1)$$

so that $$K_1 = [R_2Pu(NO_3)_6][HNO_3]^2/[H_2Pu(NO_3)_6][RNO_3]^2$$

The distribution coefficient K_d is proportional to the ratio of the concentrations of the plutonium on the resin and in solution so that

$$K_d \propto [R_2Pu(NO_3)_6]/[H_2Pu(NO_3)_6]$$

$$\therefore \qquad K_d = \text{const.}\ [HNO_3]^{-2}$$

This relation is certainly valid for nitric acid concentrations above 1 M since in this region, the experimental slope of Fig. 1 (a log–log plot) is −1·95. This result indicates that reactions involving the species $HPu(NO_3)_6^-$ play no part.

In the region between 1 M nitric acid and the maximum K_d at 0·37 M there is a deviation from this behaviour. This may be due to excessive resin swelling; an alternative explanation, however, is the following. Since significant exchange occurred with the cation resin in this region the equilibrium

$$H_2Pu(NO_3)_6 \overset{K_2}{\rightleftharpoons} Pu(NO_3)_4 + 2RNO_3 \qquad (2)$$

must become important as the nitric acid concentration is reduced (see below). From the work of ARDEN and WOOD,[18] it seems probable that the tetranitrato complex may react with the resin by the addition process

$$Pu(NO_3)_4 + 2RNO_3 \rightleftharpoons R_2Pu(NO_3)_6$$

These authors have shown that this type of process occurs in the sorption of UO_2SO_4 on to anion exchangers, and could be expected to take place efficiently in a non-ionizing solvent. Furthermore, the result of such an addition is to give a fully co-ordinated plutonium atom, analogous to the stable $H_2Pu(NO_3)_6$; in fact, the resin complex $R_2Pu(NO_3)_6$ is that successfully postulated above as being formed by anion exchange in high acidities. If this reaction occurs, the experimental value for K_d is a combination of K_d for the two processes—exchange and addition. From the cation exchange data it is clear that at acidities above 1·0 M, the possibility of $(PuNO_3)_4$ being formed is small, so that above this acidity, the exchange process is the only one observed, with an accurate dependence of K_d on $[HNO_3]^{-2}$. In the region where $H_2Pu(NO_3)_6$ and $Pu(NO_3)_4$ can co-exist, the experimental K_d will be higher than that extrapolated from results in more concentrated nitric acid, since there will be additional take-up of plutonium on to the resin as $Pu(NO_3)_4$. The precise resultant of these two processes cannot be predicted without a knowledge of the various constants involved.

At still lower acidities hydrolysis and polymerization are likely to occur in competition with ion exchange. (See also next section.) This effect would increase with decreasing acidity and is probably the reason for the falling K_d with decreasing acidity below 0·37 M. It is also possible that any effects due to water deficiency in the system will become significant in this region.

Ion exchange between Pu(IV) *and IR*-120 (H^+) *in nitric acid solutions in butex*

In high nitric acid concentrations where the stable species is $H_2Pu(NO_3)_6$ the plutonium distribution coefficients are low for cation resin and fall off rapidly with increasing acidity. Since there is no evidence from the aqueous solution chemistry of plutonium for species such as $H_2Pu(NO_3)_5^+$, it is suggested that in butex the cationic species arise from dissociation to $Pu(NO_3)_4$ followed by further dissociation to $(Pu(NO_3)_3^+)(NO_3^-)$ and possibly lower nitrato complexes:

i.e.
$$H_2Pu(NO_3)_6 \overset{K_2}{\rightleftharpoons} Pu(NO_3)_4 + 2HNO_3 \qquad (2)$$

$$Pu(NO_3)_4 \overset{k_1}{\rightleftharpoons} Pu(NO_3)_3^+ + NO_3^-$$

For the nth dissociation of $Pu(NO_3)_4$

$$Pu(NO_3)_{5-n}^{(n-1)+} \overset{k_n}{\rightleftharpoons} Pu(NO_3)_{4-n}^{n+} + NO_3^-$$

$$\therefore \quad [Pu(NO_3)_{4-n}^{n+}] = k_n[Pu(NO_3)_{5-n}^{(n-1)+}]/[NO_3^-]$$

$$= k_1 \ldots k_n[Pu(NO_3)_4]/[NO_3^-]^n \qquad (3)$$

$$= k_1 \ldots k_n K_2[H_2Pu(NO_3)_6]/[HNO_3]^2\,[NO_3^-]^n$$

[18] T. V. ARDEN and G. A. WOOD, *J. Chem. Soc.* 1596 (1956).

The reaction of the nth species with the resin will be

$$Pu(NO_3)_{4-n}^{n+} + nHR \xrightleftharpoons{K_3} Pu(NO_3)_{4-n}R_n + nH^+ \quad (4)$$

$$\therefore \quad K_3 = [Pu(NO_3)_{4-n}\,R_n][H^+]^n/[Pu(NO_3)_{4-n}^{n+}][HR]^n \quad (5)$$

$$= [Pu(NO_3)_{4-n}\,R_n][H^+]^n\,[NO_3^-]^n[HNO_3]^2/k_1 \ldots k_n K_2[H_2Pu(NO_3)_6][HR]^n$$

from which it can be shown as before that

$$K_d = \text{const.}\,[HNO_3]^{-(n+2)}$$

Fig. 2 shows that for nitric acid concentrations above 0·5 M the slope of the log–log plot is 3·3, so that to the nearest integer, the species reacting with the resin is $(Pu(NO_3)_3^+)(NO_3^-)$. The deviation from linearity of the lowest value of K_d is probably not significant. Between 0·5 M and the maximum at 0·37 M nitric acid the slope increases indicating possible exchange with the lower nitrates (e.g. $Pu(NO_3)_2^{2+}(NO_3^-)_2$) which would be expected to be formed more easily at lower acidities.

The maximum value of K_d occurs at 0·37 M nitric acid, exactly as in the anion exchange results. From the colour changes discussed previously[4] we associate these maxima with changing species; $H_2Pu(NO_3)_6$ is no longer stable, the brown colour of concentrated solutions at this acidity being due to $Pu(NO_3)_4$ and its derivatives. Cation exchange equations based on $Pu(NO_3)_4$ give $K_d \propto [HNO_3]^{-n}$ but in fact the experimental results show a positive exponent. It therefore seems that when $H_2Pu(NO_3)_6$ has completely dissociated, the resulting $Pu(NO_3)_4$ has no inherent stability to hydrolysis in butex and a rapid fall in cation exchange occurs from the same acidity as for anion exchange. In fact the shapes of the two curves are quite similar, suggesting that the absorption is almost independent of the nature of the absorbent. Sorption from butex solutions at these acidities has also been observed with finely divided crystalline materials such as copper sulphate and calcium chloride.[19]

Ion exchange between Pu(IV) *and Ir*-120 (H^+) *in perchloric acid solutions in butex containing trace nitrate*

No perchlorato complexes of plutonium are known in aqueous solution,[20] indicating that the stability constants for such complexes must be very much smaller than for the nitrato complexes. Since the ratio of the stability constants will almost certainly be similar in butex, perchlorato complexes need not be considered as long as $[NO_3^-]$ (total) $\gg$ [Pu]. From the colour of the solutions[4] there is no evidence for the existence of $H_2Pu(NO_3)_6$ species in perchloric acid–butex media.

If one attempts to ignore the presence of the small amount of nitrate and to treat the cation exchange as a normal competition between plutonium and hydrogen ions for resin sites, the usual result is obtained in which K_d decreases with increasing acidity. This, from Fig. 3, is obviously not what actually occurs. We therefore assume that plutonium is present as nitrato complexes, whose reaction with the resin can be treated as in the previous section, but tha[illegible]e situation is complicated slightly by the presence of a large excess of perchloric acid.

For the mineral acids present

$$K_N = [H^+][NO_3^-]/[HNO_3] \quad (6)$$

$$K_P = [H^+][ClO_4^-]/HClO_4],$$

[19] D. G. Tuck and G. A. Welch. Unpublished results (1956).

[20] J. C. Hindman, *The Actinide Elements*, NNES, Plutonium Project Record, Div. IV Vol. 14 A p. 335. McGraw-Hill, New York (1954).

and since electrical neutrality must be maintained

$$[H^+] = [NO_3^-] + [ClO_4^-]$$

i.e. $$[H^+]^2 = [H^+][NO_3^-] + [H^+][ClO_4^-] = K_N[HNO_3] + K_P[HClO_4]$$

Substituting for $[H^+]$ in equation (6) and re-arranging we have

$$[NO_3^-] = K_N[HNO_3]/(K_N[HNO_3] + K_P[HClO_4])^{\frac{1}{2}} \quad (7)$$

Under the experimental conditions $[HClO_4] \gg [HNO_3]$, except for the very lowest perchloric acid concentrations, and since K_P is certainly of the same order as K_N, if not larger,[21] equation (7) simplifies to

$$[NO_3^-] = K_N[HNO_3]/K_P[HClO_4]^{\frac{1}{2}} \quad (8)$$

The nth dissociation of $Pu(NO_3)_4$ can then be written by combining equations (8) and (3), as

$$\frac{[Pu(NO_3)_{4-n}^{n+}]}{[Pu(NO_3)_4]} = \frac{k_1 \ldots k_n (K_P[HClO_4])^{n/2}}{(K_N[HNO_3])^n}$$

The amount of nitric acid added was the same in each experiment, and provided that the acid is un-ionized, which must be the case in the presence of a large excess of perchloric acid, we can simplify this to

$$[Pu(NO_3)_{4-n}^{n+}]/[Pu(NO_3)_4] = \text{const. } [HClO_4]^{n/2}$$

Assuming that K_d is proportional to this ratio, we have $K_d \propto [HClO_4]^{n/2}$. The experimental results plotted as log K_d against log $[HClO_4]$ in Fig. 3 show a slope of 1·9 above about 0·5 M acid, from which we deduce that the species going on to the resin is Pu^{4+}. Below 0·5 M acid the linearity no longer holds and there may be a number of reasons for this; the simplifying assumption that $[HClO_4] \gg [HNO_3]$ is no longer valid and at these concentrations the ionization of both nitric and perchloric acids may become appreciable. Furthermore, as is shown by colour changes in more concentrated solutions of plutonium,[4] hydrolysis and polymerization occur at these acidities, so that the exact condition of the plutonium species becomes impossible to predict.

Ion exchange between Pu(IV) *and IRA*-400 (ClO_4^-) *in perchloric acid solutions in butex containing trace nitrate*

As shown in Table 1 exchange in this system is extremely low over the whole acid range studied. This confirms that no anionic complexes of plutonium are formed in perchloric acid solution in butex, a fact assumed in the previous section. The small K_d values found are probably attributable to the presence of small amounts of hydrolysed plutonium which adsorb on to the resin without exchanging. This is probably true at the highest acidity studied since, as noted above, $Pu(NO_3)_4$ species appear to have no great stability in butex. The amount of hydrolysis involved would, of course, be negligible in the cation exchange results discussed above.

Acknowledgments—We wish to thank E. F. KEMP for suggesting this problem. This paper is published by permission of the Managing Director, Industrial Group, United Kingdom Atomic Energy Authority.

[21] E. RUDZITIS and J. W. IRVINE, JR., Massachusetts Institute of Technology Laboratory for Nuclear Science, Progress Report, Feb. 1958.

J. Inorg. Nucl. Chem., 1959, Vol. 9, pp. 311 to 314. Pergamon Press Ltd. Printed in Northern Ireland

THE REDUCTION OF IODOPENTAMMINECOBALT(III) IODIDE AND POTASSIUM HEXACYANOCOBALTATE(III) WITH POTASSIUM IN LIQUID AMMONIA*

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Abstract—The reduction of $[Co(NH_3)_5I]I_2$ with potassium in liquid ammonia at $-33{\cdot}5°$ has been shown to proceed directly to elemental cobalt without evidence for intermediation of oxidation states of $Co^{<3+}$. By the reduction of $K_3[Co(CN)_6]$, the previously assumed compound of cobalt in the 1+ oxidation state, $K_3[Co(CN)_4]$, has been isolated and identified. Complete directions are given for the construction of unusually versatile equipment for use in carrying out reactions in liquid ammonia at or below its normal boiling point.

EARLIER reports from this laboratory have shown that the reduction of bromopentammineiridium(III) bromide[1] with potassium in ammonia at $-33{\cdot}5°$ yields the dimer of pentammineiridium(O), whereas similar reduction of the corresponding rhodium salt[2] results only in the precipitation of elemental rhodium. In view of these results it was of interest of determine the course of the reaction involving the 3*d* series analog, and iodopentamminecobalt(III) iodide was used because of its more favourable solubility as compared with the bromide. The experimental data given below show that the behaviour of the cobalt and rhodium salts are essentially identical, i.e,,

$$[Co(NH_3)_5I]I_2 + 3K^+ + 3e^- \rightarrow Co + 3KI + 5NH_3 \qquad (1)$$

and as soon as any cobalt is formed by reaction (1), the cobalt-catalysed[3] interaction of potassium with the solvent results in the concurrent generation of hydrogen and potassium amide. The data also show that the rates of any potentially complicating reactions between potassium amide and the original iodide are not competitive.

Also, in an earlier report from this laboratory, evidence obtained from potentiometric titrations of potassium hexacyanocobaltate(III) with potassium in liquid ammonia was interpreted as indicative of the intermediation of potassium tetracyanocobaltate(I) in the ultimate reduction to potassium tetracyanocobaltate(O).[4] Since, however, this proposed intermediate was not isolated, the experiments described below were designed to provide for the unequivocal identification of this product.

Work on both of these problems was not undertaken earlier owing to limitations of the equipment available then. The starting materials are characterized by low rates of solution and the nature of the reduction products is such that scrupulous

* This work was supported in part by the Atomic Energy Commission, Contract AT-(40-1)-1639.

(1) G. W. WATT and P. I. MAYFIELD, *J. Amer. Chem. Soc.* **75**, 6178 (1953).
(2) G. W. WATT, A. BROODO, W. A. JENKINS and S. G. PARKER, *J. Amer. Chem. Soc.* **76**, 5989 (1954).
(3) G. W. WATT, W. F. ROPER and S. G. PARKER, *J. Amer. Chem. Soc.* **73**, 5791 (1951).
(4) G. W. WATT, J. L. HALL, G. R. CHOPPIN and P. S. GENTILE, *J. Amer. Chem. Soc.* **76**, 373 (1954); Cf., W. HIEBER and C. BARTENSTEIN, *Naturwissenschaften* **13**, 300 (1952).

exclusion of both water and oxygen are essential. For example, potassium tetracyanocobaltate(I) is so sensitive to oxygen that this salt must be formed in a reaction vessel of such compact design that it can be transferred to a dry box and opened in an inert oxygen-free atmosphere. Since, following verbal descriptions of this equipment, we have had numerous requests for details of the design, it seems worthwhile to describe this equipment in sufficient detail to permit its duplication.

EXPERIMENTAL

Iodopentamminecobalt(III) iodide was prepared in 93 per cent yield by the method of YALMAN.[5] Absence of hexamminecobalt(III) ion was demonstrated by a negative oxalate test.[6] (Found: Co, 11·2; I, 72·2; N, 13·5. Calc. for $[Co(NH_3)_5I]I_2$: Co, 11·2; I, 72·5; N, 13·4%). X-ray diffraction data for this compound are given in Table 1. Potassium hexacyanocobaltate(III) was prepared in 71 per cent yield as described by BIGELOW.[7] (Found: Co, 17·5; N, 25·2. Calc. for $K_3[Co(CN)_6]$: Co, 17·7; N, 25·3%). X-ray diffraction data are included in Table 1. Potassium was purified and transferred in the manner described elsewhere.[8] All reactions in liquid ammonia were carried out in the equipment that is described in detail below.

TABLE 1.—X-RAY DIFFRACTION DATA*

$[Co(NH_3)_5I]I_2$		$K_3[Co(CN)_6]$	
d (Å)	I/I_0	d (Å)	I/I_0
5·35	0·10	6·63	0·02
3·83	1·00	5·86	0·05
2·72	0·60	5·15	0·20
2·22	0·50	4·08	1·00
1·93	0·20	3·69	0·02
1·73	0·20	3·33	0·02
1·45	0·10	3·04	0·90
1·30	0·02	2·92	0·90
1·22	0·02	2·61	0·90
1·17	0·02	2·17	0·10
1·07	0·02	2·07	0·50
		1·86	0·10
		1·84	0·40

* CuK_{α_1} radiation; tube voltage, 35 kV; filament current, 15 mA; exposure time, 6 hr.

Reduction of iodopentamminecobalt(III) *iodide*

In order to demonstrate that this salt dissolves in ammonia without solvolysis, 0·2 g of the olive-yellow salt was dissolved in 10 ml of anhydrous liquid ammonia at −78°. Practically all of the solid dissolved as the temperature was raised to −33·5° to form an orange coloured solution from which an orange coloured crystalline solid was obtained upon complete elimination of the solvent followed by drying at 33° and 0·31 mm. This solid gave a negative oxalate test for hexamminecobalt(III) ion. (Found: N, 15·5. Calc. for $[Co(NH_3)_5I]I_2 \cdot NH_3$: N, 15·5%). Despite the rather striking colour change that results from recrystallization of the iodide from liquid ammonia it is believed that retention of solvent in a quantity that corresponds exactly to a 1-ammoniate is

[5] R. G. YALMAN, *J. Amer. Chem. Soc.* **77**, 3219 (1955).
[6] J. BJERRUM and J. P. MCREYNOLDS, *Inorganic Syntheses* Vol. 2, p. 220. McGraw-Hill, New York (1946).
[7] J. H. BIGELOW, *Inorganic Synthesis* Vol. 2, p. 225. McGraw-Hill, New York (1946).
[8] G. W. WATT and D. M. SOWARDS, *J. Amer. Chem. Soc.* **76**, 4742 (1954).

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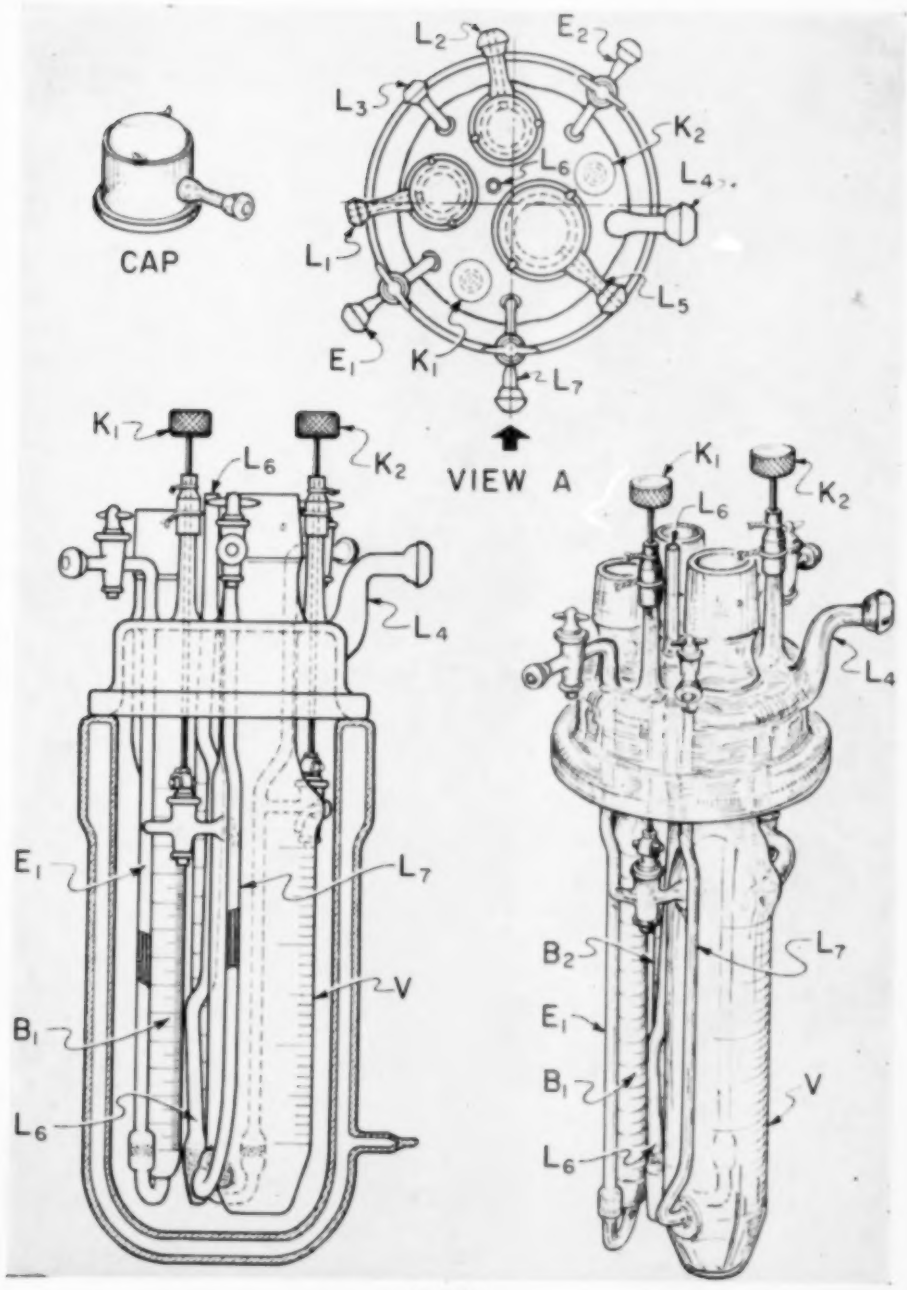
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FIG. 1(A).

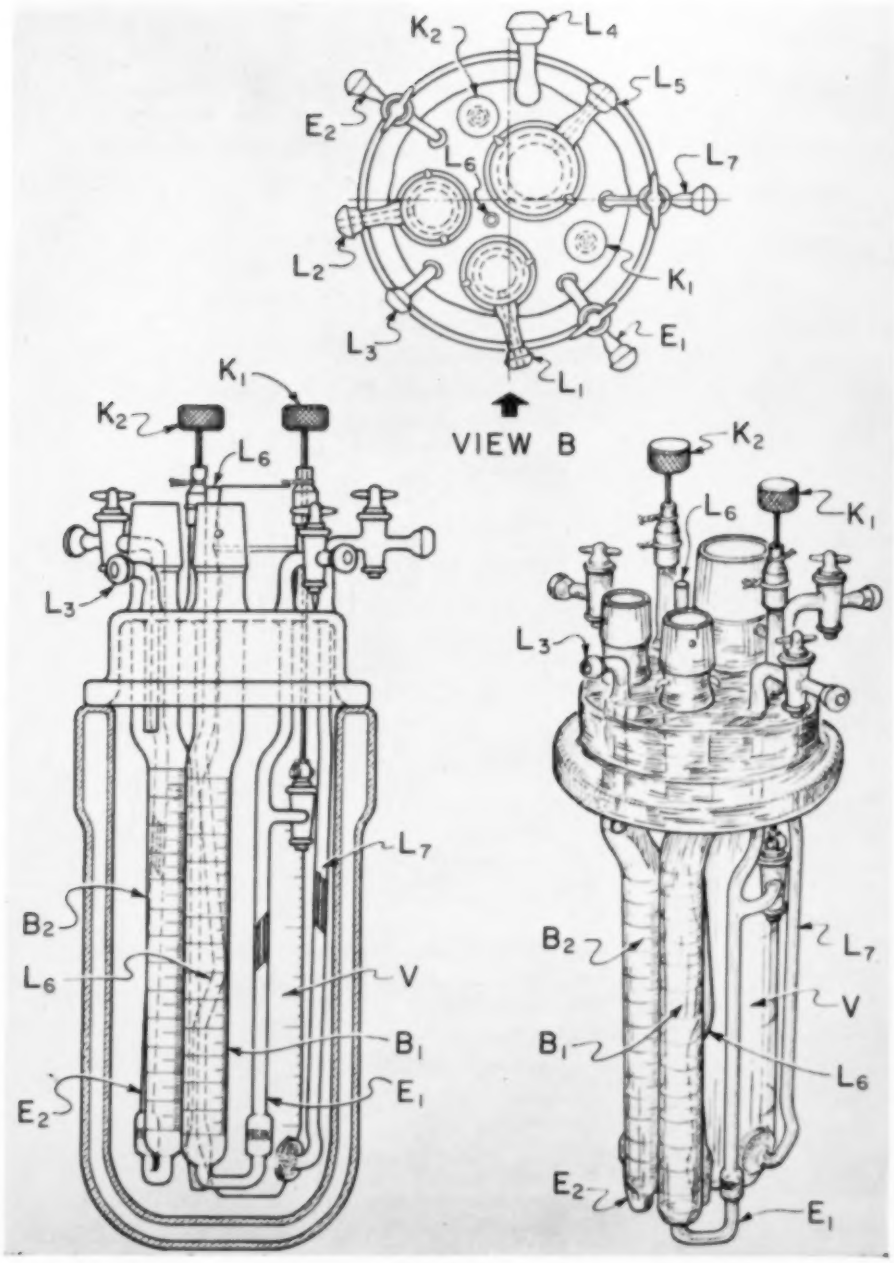

FIG. 1(B).

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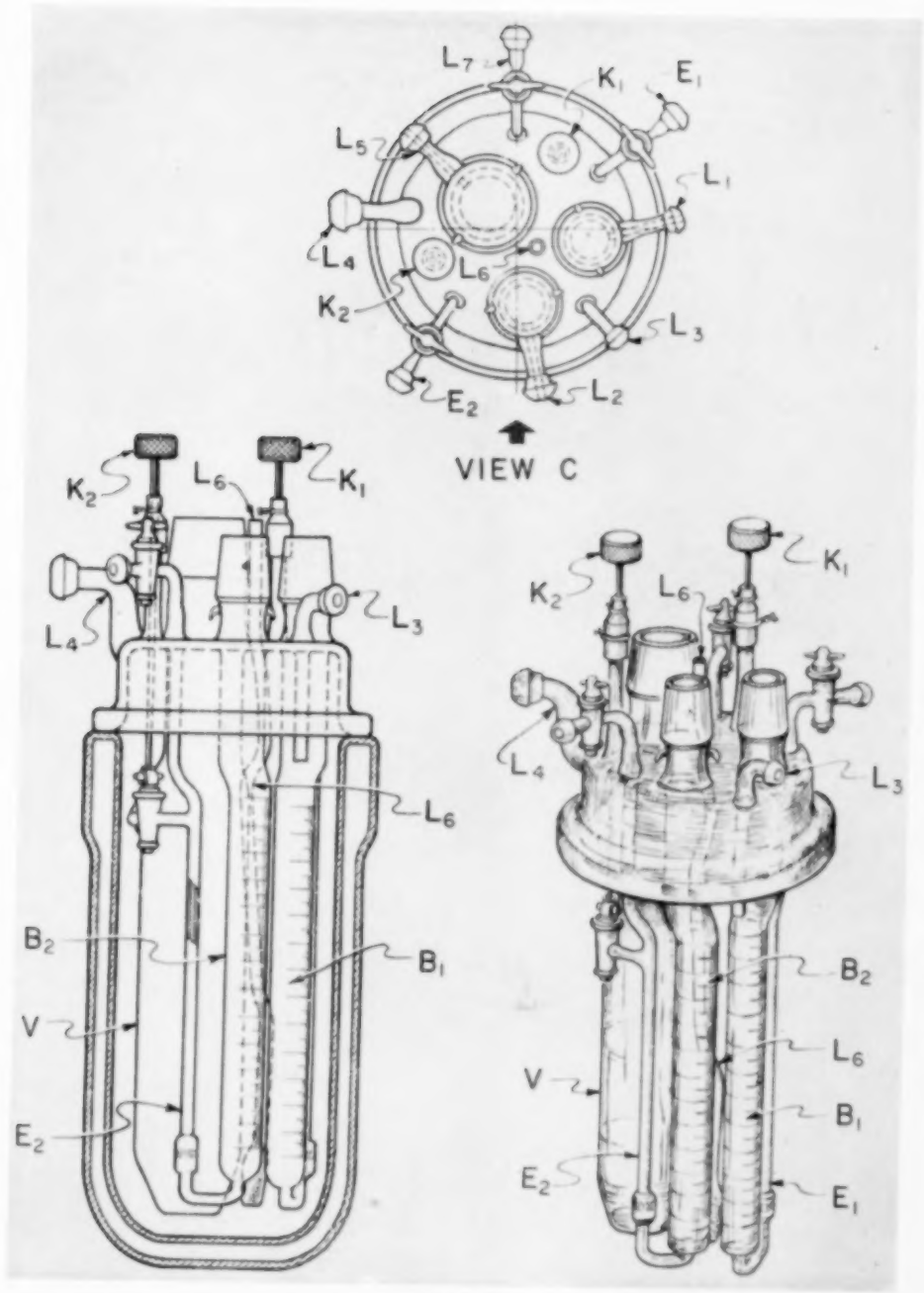
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FIG. 1(C).

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entirely fortuitous since the X-ray diffraction pattern for this product was substantially identical with that for iodopentamminecobalt(III) iodide.

In a typical reduction reaction, 1·471 g (2·80 mmoles) of the iodide was dissolved completely in 120 ml of ammonia over a period of 2·5 hr and treated dropwise with a solution of 0·4703 g (12·03 mmoles) of potassium in 25 ml of ammonia. The colour of the solution changed from orange to red to yellow as a black precipitate formed and hydrogen evolution was observed after addition of the first few drops of potassium solution. A total of 40·4 cc (1·80 mmoles) of hydrogen was collected; this is equivalent to 3·60 mmoles of potassium and, accordingly, 8·43 mmole of potassium was consumed in the reduction of the cobalt salt, and K/Co = 3·01. The black solid product was washed eight times with 100 ml portions of ammonia; following evaporation of the solvent from the combined filtrate and washings, analysis of the residue accounted for 1·059 g of iodine, or 99·3 per cent of that used as iodopentamminecobalt(III) iodide. The reaction vessel containing the black solid product was transferred to a dry box and opened in an inert oxygen-free atmosphere, and a 0·0572 g sample was taken for analysis. (Found: Co, 99·7%.) Of the total cobalt used initially as the iodide, 99·8 per cent was accounted for as elemental cobalt. This product was highly pyrophoric; upon controlled exposure to dry air, a sample was oxidized to cobalt(III) oxide. (Found: Co, 70·5. Calc. for Co_2O_3: Co, 71·1%).

Reduction of potassium hexacyanocobaltate(III)

In a representative case, 1·0063 g (3·023 mmoles) of $K_3[Co(CN)_6]$ was reduced with 18 ml of 0·1336 molar potassium solution. Upon addition of successive increments of potassium, the solution assumed a pale yellow colour and a pale yellow gelatinous and very voluminous precipitate[4] separated. This solid was washed eight times with 100 ml portions of ammonia, residual solvent was removed *in vacuo* and the reaction vessel containing the solid reaction product was transferred to a dry box and opened in an inert oxygen-free atmosphere. (Found: Co, 20·8; K, 42·0; N, 19·4. Calc. for $K_3[Co(CN)_6]$: Co, 21·1; K, 41·8; N, 20·0%). When this originally pale yellow solid was warmed to room temperature, its colour changed to red-brown; upon exposure to even traces of air, the solid decomposed extremely rapidly and exothermally to form a black solid that was not further investigated.

Equipment

The kinds of reaction vessels (i.e., exclusive of connecting lines and accessory equipment) that have been used in carrying out reactions in liquid ammonia at or below its normal boiling point have been similar in most respects to the equipment described by FERNELIUS and JOHNSON.[9] Although numerous modifications[10,11] have been incorporated, all of the resulting reaction vessels have entailed limitations of the type encountered in the present studies and referred to above. Accordingly, the equipment assembly described in detail below was designed and found to be highly satisfactory.

The equipment consists of an unsilvered flat-bottom dewar flask 3·75 in. inside diameter and 8·25 in. inner depth, and 8·75 in. over-all height. The shoulder of the dewar flask is flat and has a ground glass surface ca. 0·4 in. wide. A flanged all-glass head also having a ground glass under surface is fitted to the dewar flask and carries all of the other essential parts of the apparatus. A top view of the head is shown in Fig. 1A which includes also both projectional and pictorial side views. Figs. 1B and 1C are related in that they represent successive ninety degree counter-clockwise rotations from the position corresponding to Fig. 1A.

With reference first to Fig. 1A, L_3 is the refrigerant liquid ammonia inlet line (8 mm inside diameter) which bears the male portion of a 12/5 ball and socket joint* for attachment to the source of supply of refrigerant. The exit end of this tube should extend ca. 0·5 in. below the flange. L_4 (10 mm inside diameter) is the gas exit line and terminates in an 18/9 ball for attachment to the line leading to the ammonia absorbers. L_1 and L_2 (8 mm inside diameter) are the anhydrous ammonia exit lines from calibrated burettes B_1 and B_2. These lines enter ground glass caps (24/40) that can

* With the single exception of the ball and socket joint on line L_4, all of the others shown conform to this same specification.

[9] W. C. FERNELIUS and W. C. JOHNSON, *J. Chem. Educ.* **6**, 445 (1929).
[10] G. W. WATT and T. E. MOORE, *J. Amer. Chem. Soc.* **70**, 1197 (1948).
[11] G. W. WATT and C. W. KEENAN, *J. Amer. Chem. Soc.* **71**, 3833 (1949).

be rotated and thus serve in lieu of stopcocks; a pictorial view of one of these caps is shown as an inset to Fig. 1A. L_5 is an identical line leading through a ground glass cap (34/45) that serves as the top closure for the main reaction vessel, V, which is graduated and calibrated. The line L_6 is an inlet line (8 mm inside diameter) for the pre-dried air that is used to stir the refrigerant ammonia; this line terminates in a coarse porosity gas dispersion frit. L_7 is the filtrate exit line (8 mm outside diameter, 2 mm capillary) from V. This line also terminates in a 12/5 ball just preceded by a semi-micro stopcock.* K_1 and K_2 are knurled 304 stainless steel knobs attached to the tops of stainless steel rods that terminate in saddles that fit over the stopcocks between burettes B_1 and B_2 and V. The entry of these steel rods through glass tubes in the head is made gas-tight by the use of rubber sleeves. (A more elegant but no more useful version of this connexion involves the use of a ball and socket joint and a metal to glass seal.) The relative positions of the components carried by the head piece are dictated by the necessarily compact arrangement of the parts that must be accommodated within the dewar flask.

Lines E_1 and E_2 are 8 mm outside diameter 2 mm capillary inlet lines to burettes B_1 and B_2. In addition to the ball joints and stopcocks on the portions of these lines that project above the head, these lines include medium porosity† fritted glass filter discs (10 mm diameter) positioned as shown in Fig. 1. As is also evident from the illustrations, these lines are connected to V via stopcocks that are operated‡ via K_1 and K_2. Thus, by exerting a pressure of ammonia gas on the surface of solutions contained in B_1 and B_2, known volumes may be filtered and transferred via E_1 and E_2 to V. In a similar manner solutions in V may be either filtered or decanted through the 20 mm diameter medium porosity fritted glass filter disk between V and L_7. The position of this filter above the bottom of V (ca. 6 mm in the present case) can be determined only in relation to the nature of the substances to be separated. For example, for gelatinous or other solids that tend to clog the filter, the position of the filter should be such that the solids may be allowed to settle below the bottom of the filter and the supernatant solution and/or washings may be decanted. It also should be noted that the bottom of V is flat in order better to accommodate a magnetic stirrer bar§ and that V is tapered at the bottom as a means of minimizing liquid hold-up. The volume of the calibrated section of V is 170 ml; the optimum range of solution volumes is 75–100 ml.

With regard to the accessory equipment, details of manipulation, etc., further comment here is not considered necessary in the light of details included in earlier publications.[9,10,11] It should be pointed out however that the experiments described above did not require an apparatus that includes two burettes for the preparation and transfer of reactants. A somewhat similar equipment piece employing only one burette can be constructed with less severe restrictions on reaction vessel size in relation to the total available space. The equipment described above was designed for maximum flexibility; it is noteworthy for example that this equipment can be used in carrying out potentiometric titrations in liquid ammonia[12,13] with the added and distinct advantage of providing for both separation and purification of the products.

Acknowledgement—We wish to acknowledge our indebtedness to MR. J. R. HOLMES for the preparation of the illustration copy.

* Although Corning No. 7320 (Catalog LG-1) micro stopcocks may be used, we have found that the Scientific Glass Apparatus Co.'s semi-micro stopcock No. MO-535 (a non-stock item) is much more satisfactory. All of the stopcocks shown in Fig. 1 are of this type.

† Either fine or coarse filters may be substituted as required by the character of the solid phases to be separated.

‡ Since these stopcocks are submerged in liquid ammonia at −33·5°, lubrication with Dow–Corning high vacuum silicone grease is necessary for ease of manipulation.

§ It has been our experience that seamless Teflon Alnico V stirring bars (Halogen Insulator and Seal Corporation) are most satisfactory.

[12] G. W. WATT and J. B. OTTO, JR., *J. Electrochem. Soc.* **98**, 1 (1951).
[13] G. W. WATT and D. M. SOWARDS, *J. Electrochem. Soc.* **102**, 46, 545 (1955).

J. Inorg. Nucl. Chem., 1959, Vol. 9, pp. 315 to 317. Pergamon Press Ltd. Printed in Northern Ireland

THE DIFFERENT SOLUBILITY BEHAVIOUR OF THE ISOSTERIC LIQUIDS CO AND N_2 IN LIQUID OZONE*

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The Research Institute of Temple University, Philadelphia, Pennsylvania

(*Received* 20 *August* 1958)

Abstract—In spite of the close similarity of CO and N_2 in their physical properties, they show an unexpected solubility behaviour in liquid ozone. CO is miscible in all proportions at 77·4°K with liquid O_3, while N_2 in O_3 and vice versa show very limited solubility. A preliminary ternary composition diagram of the system liquid O_2–N_2–O_3 at 77·4°K is given.

A FEW years ago it was shown at our laboratories[1] that liquid CO is miscible with liquid O_2 in all proportions. This was to be expected since CO and N_2 are a typical example of Langmuir's concept of isosteric molecules and because liquid N_2 and O_2 (liquid air!) are miscible in all proportions.

It was found that liquid CO and liquid O_3 are miscible in all proportions, producing a homogeneous highly detonating liquid.† (Its colour is a direct function of its composition, ranging all the way from the colourless CO to the deep blue colour of O_3.) Surprisingly, however, liquid N_2 and ozone are not miscible. The system liquid N_2–liquid O_3 shows even less mutual solubility than the system liquid O_2–liquid O_3.

The mutual solubilities of the above three binary systems with liquid ozone, at 77·4°K, are given in Table 1.

TABLE 1.—COMPOSITIONS IN MOLE PER CENT AT THE BOUNDARY AT 77·4°K

	Ozone-rich phase	Ozone-poor phase
$CO + O_3$	Miscible in all proportions	
$O_2 + O_3$[2,3]	15·7% O_2 : 84·3% O_3	93·1% O_2 : 6·9% O_3
$N_2 + O_3$	8·8(±0·9)% N_2 : 91·2% O_3	95·59% N_2 : 4·41(±0·14)% O_3

The solubility of ozone in liquid nitrogen was also determined at 81·8°K and found to = 5·1 mol % O_3; the solubility of O_2 in O_3 at the same temperature = 7·3 mol per cent. Within experimental error the solubility of ozone in nitrogen, as a function of temperature, parallels that of the oxygen–ozone system and hence it is to be expected that their critical consolute temperature will be higher than that for the O_2–O_3 system which = 93·2°K.

* This work sponsored by the Army Ballistic Missile Agency, Redstone Arsenal, Alabama.

† A very slow, and for our purposes, negligible oxidation of CO to CO_2 was observed in the liquid CO—O_3 system at 77·4°K; in 4 hr only 0·03 mol % CO was oxidized.

[1] A. V. GROSSE, A. D. KIRSHENBAUM and A. G. STRENG, *J. Amer. Chem. Soc.* **79**, 6341 (1957); A. D. KIRSHENBAUM, *Final Report on Fundamental Studies of New Explosive Reactions for Office of Ordnance Research*, Contract No. DA-36-034-ORD-1489, Project No. TB2-0001(916), Research Institute of Temple University (1956).
[2] A. C. JENKINS, F. S. DIPAOLO and C. M. BIRDSALL, *J. Chem. Phys.* **23**, (1955).
[3] C. BROWN, A. W. BERGER and C. K. HERSH, *J. Chem. Phys.* **23** ,1340 (1955).

The method used was simple. A known volume of pure ozone *gas* (measured at S.T.P.), was condensed and successive amounts of N_2 condensed upon it and measured as a *liquid* at 77·4°K, until the deep blue lower ozone layer disappeared completely. Conversely, to determine the conjugate point, a known volume of N_2 *gas* (measured at S.T.P.), was dissolved in successive amounts in pure *liquid* ozone, measured as a liquid, until a trace of a nearly colourless line of the nitrogen-rich upper layer appeared above the deep blue liquid ozone.

An all glass apparatus was used. All stopcocks were greased with Kel-F grease; a 1–2 cm layer of Kel-F oil was placed over the mercury in the manometer. Mixing was achieved by simple shaking or, for larger samples, by means of a hand operated magnetic stirrer.

HILDEBRAND's highly useful concept of solubility parameters,[4] or δ_T, does not predict the observed different behaviour of CO and N_2 in O_3. δ_T, is defined[4] by the equation:

$$\delta_T = \frac{\Delta H_T - RT}{V_T}$$

where ΔH_T is the molar heat of vaporization and V_T the molar volume of the liquid, both at T°K. The solubility parameters of the three compounds and other pertinent data are given in Table 2.

TABLE 2

	T_b (= N.B.P.) (°K)	V_{T_b} (cm³/mole)	ΔH_{T_b} (kcal/mole)	δ_T ([cal/cm³]$^{1/2}$)
O_2	90·19	28·0	1·630	7·2
N_2	77·35	34·6	1·330	5·9
CO	81·66	34·4	1·440	6·1
O_3	161·3	29·70*	3·495	10·61*

* At 77·4°K.

A perusal of Table 2 demonstrates immediately the close similarity of the physical properties of N_2 and CO. According to HILDEBRAND's theory,[4] the critical consolute temperature of two liquids is essentially proportional to the square of the difference of their solubility parameters. On this basis, one would expect the CO–O_3 system to have a consolute temperature higher than the O_2–O_3 system ($T_C = 93{\cdot}2$°K) and slightly below the N_2–O_3 system. Actually (see Table 1), CO and O_3 are already completely miscible at 77·4°K.

In view of the close similarity of the isoelectronic CO and N_2, which persists even in their molecular spectra, a simple explanation for this difference is not available. As pointed out by PITZER,[5] a much more detailed consideration of various special interacting forces, such as are due to the triplet electronic state of the O_2 molecule

[4] J. H. HILDEBRAND and R. L. SCOTT, *The Solubility of Non-electrolytes* (3rd Edition). Reinhold, New York (1950).
[5] K. S. PITZER, Private communication.

(which will tend to raise T_C for O_2–O_3) and the polarizabilities of CO, N_2 and O_2, will have to be taken into account for a theory to be successful.

In view of the low solubility of N_2 in O_3 a small addition of N_2 to the single phase ozone rich O_3–O_2 mixture causes separation into two phases. Thus the addition of

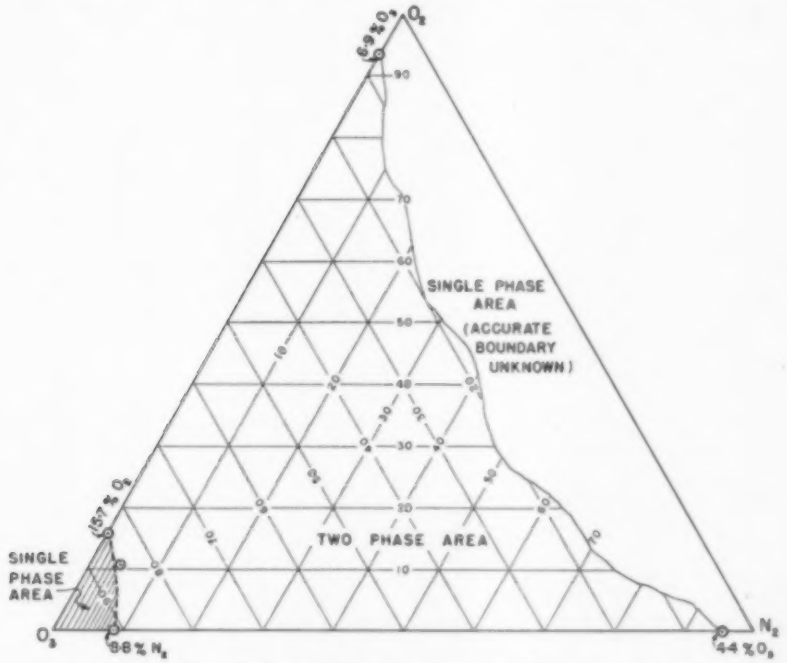

FIG. 1.—Phase diagram of O_3–O_2–N_2 system at 77·4°K, in mol per cent.

4·34 mol % N_2 to a single phase O_2–O_3 solution, of 11·3 mole % O_2 and 88·7 mol % O_3, at 77·4°K, precipitates an ozone rich lower layer and slightly blue coloured ozone poor oxygen-nitrogen layer.

A preliminary ternary composition diagram at 77·45°K can now be drawn from the three points mentioned above. It is shown in Fig. 1. As can be seen, the single phase area of the system O_3–O_2–N_2 is very limited. In experimental work with ozone-rich oxygen mixtures, inadvertent admission of air or nitrogen will cause a homogeneous solution to separate into a dangerous two phase system.

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LETTER TO THE EDITORS

Alkali and alkaline earth rhenides*

(*Received* 22 *January* 1959)

A FEW years ago one of us reported, in W. Noddack's Sixtieth Birthday Celebration issue,[1] the isolation of lithium rhenide. It was obtained by the reduction of an aqueous $KReO_4$ solution with metallic lithium.

Shortly before, KLEINBERG *et al.*[2] had described a solid rhenium mixture, prepared by the reduction of an ethylene diamine-water solution of $KReO_4$ with metallic potassium. They subsequently published additional information[3] on the method and properties of the rhenide. However, their purest preparation,[3] described as a grey solid, contained 68·5 mol % $KRe \cdot 4H_2O$ and 31·5 mol % KOH, besides a "small and variable (about 1–2%) content of organic material, presumably ethylenediamine, has been neglected in the calculations".

A number of *pure* alkali and alkali earth rhenides have now been *isolated* and *analysed*. Lithium, sodium, potassium, strontium and barium rhenides, form colourless, crystalline, thermally stable salts. They are very soluble in water. The potassium salt can be obtained in millimeter long prisms. The aqueous solutions exhibit basic properties. They are quite stable in an inert atmosphere and in an alkaline solution but oxidize slowly in the presence of O_2. At a pH below 7 they decompose into hydrogen and a black precipitate, consisting, presumably, of rhenium metal. Rhenide ion reduces aqueous solutions of $[Cu(NH_3)_4]^{2+}$, $[Ag(NH_3)_2]^+$ and $[Bi(OH)_4]^-$ immediately to metallic Cu, Ag and Bi.

New methods of isolation and purification have been developed which have been used to prepare pure rhenides, from either lithium[1] or potassium[2,3] reductions, so that gram quantities of rhenides can now be produced easily.

Outside of the LiOH-LiRe fractional crystallization[1] the two methods are:

(1) Lithium phosphate precipitation. The large excess of lithium hydroxide can be eliminated from a rhenide solution by precipitation with diammonium phosphate solution, filtration, evaporation to dryness and recrystallization.

(2) Ion exchange separation of lithium, sodium or potassium hydroxide from the rhenide and preparation of any desired rhenide by addition of suitable hydroxide solution to the $[NH_4]Re$ solution.

In method "2" the rhenide + alkali hydroxide solution, after most of the LiOH had been removed by recrystallization[1] or most of KOH by extraction with anhydrous *iso*propanol,[2,3] was passed slowly through an ion exchange column, filled with the strong sulfonic acid cation exchange resin—Amberlite IR-120 (Rohm & Haas) in its ammonium form. The effluent obtained consisted of an ammonium rhenide and ammonia solution, produced according to the following equation:

$$[NH_4]^+\left[-\begin{matrix}|\\R\cdot SO_3\\|\end{matrix}\right]^- + Li^+[Re(H_2O)_4]^- + LiOH \rightarrow [NH_4]^+[Re(H_2O)_4]^- + NH_3 + H_2O + Li^+\left[-\begin{matrix}|\\R\cdot SO_3\\|\end{matrix}\right]^-$$

It was checked continuously for a lithium (or Na or K) breakthrough simply by a flame test. The rhenide content of the solution was determined analytically and the stoicheiometric amount of any desired hydroxide solution added to an aliquot of the effluent.

* This research was supported by the U.S. Atomic Energy Commission. For additional results see First Annual Progress Report on the United States Atomic Energy Commission, Contract AT(30-1)-2082, Report no. NYO-2155, September 20, 1958.

[1] A. V. GROSSE, *Z. Naturf.* **8b**, 533 (1953).
[2] E. GRISWOLD, J. KLEINBERG and J. B. BRAVO, *Science* **115**, 375 (1952).
[3] J. B. BRAVO, E. GRISWOLD and J. KLEINBERG, *J. Phys. Chem.* **58**, 18 (1954).

The salt was obtained from the resulting clear colorless solution by evaporation to dryness, in vacuo, at room temperature and recrystallized from small amounts of water. Small amounts of hydroxide increase the oxidation stability of the salt.

Typical analyses of hydroxide stabilized or pure salts, are as follows:

(1) $Li^+[Re(H_2O)_4]^-$: calc.: wt. % Li 2·62 Re^- 70·22 H_2O 27·16
Mol. wt. 265·31 found: wt. % 2·80 (titr.) → 69·9 26·9
Above = 93·1 (±0·5) mol % $Li^+[Re(H_2O)_4]^-$ and 6·9 (±0·5) mol % $LiOH \cdot H_2O$

(2) $Ba^{++}[Re(H_2O)_4]_2^-$: calc.: wt. % Ba 20·99 Re^- 56·96 Total Re 56·96 H_2O 22·05
Mol. wt. 654·11 found: wt. % (titr.) 20·5 56·6 56·6 by Δ 22·9
wt. % (grav.) 20·4

Re: Ba ratio, for pure barium rhenide, Calc. 2·00; Found 2·03 (±0·03). Valence number change, Calc. 8·00; Found 8·00 (±0·05)

Rhenide was determined by permanganate titration in excess of 4 N sulphuric acid:[1] 8 equivalents of permanganate oxidize 1 equivalent of Re^-. The total rhenium content was established by oxidizing all of it to perrhenate by H_2O_2 in alkaline solution, and precipitating it as nitron or thallium perrhenate. Water was determined by heating the rhenide to 500°C; alkali by standard acid titration (back titration), and Ba also gravimetrically as $BaSO_4$.

The thermal stability of the *rhenide tetrahydrates* was higher than expected; this is a direct indication that the 4 water molecules form a *stable* covalent penetration complex with the rhenide ion. Samples of the dry salt, stabilized with ~5% hydroxide, were heated in a small tube, attached to a manometer, U-tube and gas holder. Up to 275° no noticeable reaction took place. Barium rhenide loses its co-ordination water (in 1 h) at about 300°C, forms BaO and H_2 and turns black due to metallic rhenium. The reaction is a topochemical one and propagates in a characteristic black mosaic-like pattern through the white undecomposed crystals. The thermal decomposition follows the scheme:

$$Ba^{++}[Re(H_2O)_4]_2^- \rightarrow BaO + 2Re + 7H_2O + H_2 \uparrow$$

Lithium rhenide behaves the same way, except that the decomposition temperature is about 350°. On heating to 400° all of the complex water (except the part used up in oxide and H_2-formation) can be recovered quantitatively.

A study of the structure of these rhenides is now under way.

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J. Inorg. Nucl. Chem., 1959, Vol. 9, pp. 320 to 324. Pergamon Press Ltd. Printed in Northern Ireland

NOTES

The alpha half-life of plutonium-239

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VALUES for the alpha half-life of ^{239}Pu ranging from 24,100 ± 240 years to 24,400 ± 100 years have been reported.[1] The samples of plutonium used for these half-life determinations contained appreciable quantities of ^{238}Pu and ^{240}Pu thus reducing the accuracy of the determination. Because almost isotopically pure ^{239}Pu is now available from the Heavy Element Electromagnetic Separator at Harwell, it was of interest to redetermine the alpha half-life of this isotope.

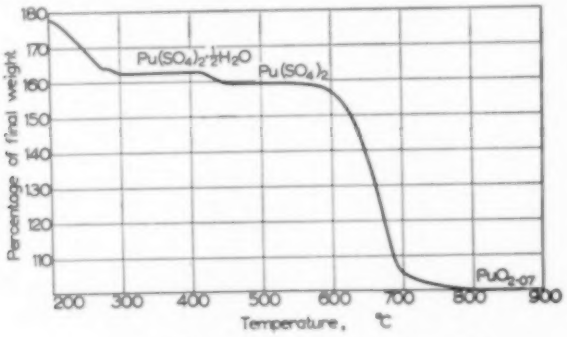

FIG. 1.—Thermogravimetric curve for $Pu(SO_4)_2$.

The isotopic content of the plutonium used for the half-life determination was as follows:—99·92% ^{239}Pu, 0·072 ± 0·003% ^{240}Pu and 0·003 ± 0·001% ^{241}Pu. The sample contained traces of other impurities, 0·08% Mg, 0·05% Na, 0·05% Fe, 0·1% Al and 0·15% Cu w/w Pu. Two compounds of plutonium, $Pu(SO_4)_2$ and $PuCl_3$, were prepared and used in the determination of the half-life of ^{239}Pu. By comparing the weight ratio of $Pu(SO_4)_2$ to its decomposition product, PuO_2, DRUMMOND and WELCH[2] found that while anhydrous $Pu(SO_4)_2$ is formed at 480°C, the sulphate did not exactly correspond to stoicheiometric $Pu(SO_4)_2$ at 450° and 520°C. At temperatures above 520°C the sulphate began to decompose. Plutonium dioxide, formed at 870°C by decomposition of the sulphate, was not stoicheiometric but had the composition $PuO_{2\cdot07}$. In the present work, the thermogravimetric behaviour of plutonium sulphate was studied with the aid of a thermogravimetric balance of sensitivity 2·277 mm/mg. The sulphate was heated at the rate of 3°C/min and readings were taken at 5°C intervals. Decomposition of the sulphate was complete at 825°C and further heating to 870°C caused no observable change in weight. A plateau was observed at 465–525°C in the thermogravimetric plot; assuming the final compound to be $PuO_{2\cdot07}$, the equivalent weight of the compound corresponding to this plateau was calculated to be 433. The theoretical equivalent weight of $Pu(SO_4)_2$ is 431. The difference between the experimental and theoretical equivalent weight, assuming the compound formed at 465–525°C to be $Pu(SO_4)_2$, is within the experimental error. No uptake of moisture occurred when the sulphate was allowed to cool from 490°C to room temperature in the relatively dry atmosphere of the thermogravimetric balance. These results essentially confirm the observations of DRUMMOND and WELCH. $Pu(SO_4)_2$, formed at 490°C, therefore appeared to be a suitable compound for use in the determination of the half-life of ^{239}Pu.

[1] *Table of Isotopes* UCRL-1928.
[2] J. L. DRUMMOND and G. A. WELCH, IGO R/W-20.

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Analysis of UCl_4 and $AmCl_3$[2] has shown that these compounds can be prepared anhydrous and stoicheiometric. It was therefore expected that $PuCl_3$ would be a suitable compound to use in the half-life determination of ^{239}Pu.

Plutonium trichloride was prepared by the action of carbon tetrachloride on plutonium oxide at 725°C.[4] The apparatus used for this preparation has been described elsewhere.[3] Three samples of plutonium trichloride were analysed for chloride ion by potentiometric titration with silver nitrate. The results showed the chloride ion content to be 99·8 ± 0·5% of the value expected for stoicheiometric $PuCl_3$.

Determination of the half-life

Plutonium sulphate. A 75 mg sample of anhydrous $Pu(SO_4)_2$ was prepared at 490°C, weighed in a dry atmosphere, dissolved in 0·001 M nitric acid and diluted to 25 ml in a calibrated standard flask. Three sources were prepared for alpha particle counting by transferring 9·925 μl samples of solution from the flask to three platinum trays. A drop of a spreading agent, tetraethylene glycol, was added to each aliquot on the tray before evaporation, in order to obtain a more uniform deposit of material. The aliquots were evaporated to dryness and heated to 600°C to remove organic matter. The sources were counted in the low-geometry proportional counter,[5] which had a geometry factor of 724·2 ± 0·8.

Two further samples of $Pu(SO_4)_2$ were prepared and the experiment repeated. The results are shown in Table 1.

TABLE 1

Experiment	Specific activity	Half-life
1	$1{\cdot}3607 \times 10^5$ α/min per μg	24,404 ± 50 years
2	$1{\cdot}3582 \times 10^5$ α/min per μg	24,448 ± 50 years
3	$1{\cdot}3592 \times 10^5$ α/min per μg	24,431 ± 50 years
	Mean value	24,427 ± 35 years

The weight of the sample of plutonium sulphate was corrected for traces of impurities. The observed α-emission from the prepared sources was corrected for ^{240}Pu and ^{241}Pu content, taking the specific activity of these isotopes to be $5{\cdot}011 \times 10^5$ α/min per μg[6] and $8{\cdot}249 \times 10^3$ α/min per μg[7] respectively. The difference between the number of disintegrations per unit time from sources prepared from the same solution was not greater than ±0·1% and the number of counts recorded from each source was such that the statistical error was not greater than ±0·1%. Errors in duplicate weighings of the sulphate were less than ±0·1%. The errors given in Table 1 were computed from all the known sources of error. The final error on the mean value was calculated from $\sqrt{\Sigma x^2/n(n-1)}$ where x is the individual error.

Plutonium trichloride. A 10 mg sample of $PuCl_3$ was prepared as described above, weighed, dissolved in 0·001 M nitric acid and the solution diluted to 5 ml in a calibrated standard flask. Three sources were prepared for alpha particle counting.

TABLE 2

Experiment	Specific activity	Half-life
4	$1{\cdot}3591 \times 10^5$ α/min per μg	24,431 ± 60 years
5	$1{\cdot}3622 \times 10^5$ α/min per μg	24,377 ± 60 years
6	$1{\cdot}3618 \times 10^5$ α/min per μg	24,384 ± 60 years
	Mean value	24,397 ± 42 years

[3] G. R. HALL and T. L. MARKIN, *J. Inorg. Nucl. Chem.* **4**, 137 (1957).
[4] S. FRIED and N. DAVIDSON, *J. Amer. Chem. Soc.* **70**, 3539 (1948).
[5] R. HURST and G. R. HALL, *Analyst* **77**, 790 (1952).
[6] M. G. INGHRAM, D. C. HESS, P. R. FIELDS and G. L. PYLE, *Phys. Rev.* **83**, 1250 (1951).
[7] S. G. THOMPSON, K. STREET, A. GHIORSO and F. L. REYNOLDS, *Phys. Rev.* **80**, 1108 (1950).

Two further samples of $PuCl_3$ were prepared and the experiment repeated. The results are shown in Table 2. A correction has been made for ^{240}Pu and ^{241}Pu.

Errors in weighing the trichloride were $\pm 0{\cdot}2\%$. It was assumed that the sublimate of $PuCl_3$ was free from traces of impurities present in the original solution. Other errors were the same as for the experiments using $Pu(SO_4)_2$.

The values calculated for the alpha half-life of ^{239}Pu using the compounds $Pu(SO_4)_2$ and $PuCl_3$ are in reasonable agreement. The calculated mean value for the specific activity is $1{\cdot}360 \pm 0{\cdot}001 \times 10^5$ α/min per μg, giving a value of 24,413 $\pm$ 30 years for the alpha half-life of ^{239}Pu.

Acknowledgements—The author wishes to thank Dr. M. L. SMITH for the loan of the plutonium sample, Mr. F. T. BIRKS for spectrographic analysis and the Mass Spectrometry Group for isotopic analyses of the plutonium.

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The preparation of solutions of radiochemically pure niobium (^{95}Nb) and zirconium (^{95}Zr)

(*Received* 9 *December* 1958)

IN recent studies[1,2] of the solvent extraction of niobium and zirconium from nitric acid solutions we have used the radioactive tracers ^{95}Nb and ^{95}Zr. These were obtained from the Radiochemical Centre, Amersham, Bucks, England, as a nominally carrier-free mixture of the two in $0{\cdot}5\%$ w/v oxalic acid. A solvent extraction method of separation and purification of zirconium using 0·05 M thenoyltrifluoroacetone has been reported,[3] but this does not give a high recovery of ^{95}Zr, or sufficient decontamination from ^{95}Nb if the zirconium is required for the accurate measurement of distribution coefficients less than 0·1 or greater than 10. The separation of ^{95}Nb and ^{95}Zr is described below by two methods which give both elements in high yield and high purity.

(1) *The separation of* ^{95}Nb *and* ^{95}Zr *by solvent extraction with thenoyltrifluoroacetone* (*TTA*)

The oxalic acid in the $0{\cdot}5\%$ oxalic acid solution of $^{95}Zr/^{95}Nb$ was destroyed by heating the solution with hydrogen peroxide and 15 M HNO_3 in a glass beaker and evaporating it down to a few millilitres under an infra-red lamp to give $^{95}Zr/^{95}Nb$ in ~15 M HNO_3. In order to reduce losses of ^{95}Nb by adsorption (i) the beaker was pre-treated with dichloro-dimethyl-silane in carbon tetrachloride to give a silicone film, and (ii) sufficient niobium carrier in oxalate solution was initially added to give a final concentration of 5×10^{-6} M Nb (this was regarded as permissible for tracer studies since the activity was sufficiently high to require a dilution by a factor of 100 before use in the actual experiments).

The 15 M HNO_3 solution of $^{95}Zr/^{95}Nb$ was then diluted to 2 M HNO_3 and the ^{95}Zr extracted into an equal volume of freshly prepared 0·5 M TTA/benzene by stirring for 5–10 min in siliconed glass apparatus. Earlier experiments with 0·05 M TTA gave only 30–40% extraction of the ^{95}Zr, but with 0·5 M TTA >95% was extracted. Stirring times >10 min increased the extraction of ^{95}Nb. These results agree with those obtained by MOORE[4] who has dealt thoroughly with the extraction of zirconium into TTA/xylene solutions. The ^{95}Nb in the aqueous phase was further purified from ^{95}Zr by five successive equal-volume equilibrations with 0·5 M TTA/benzene, when a constant distribution coefficient of ~0·01 was obtained. The solution of purified ^{95}Nb was washed with

[1] C. J. HARDY and D. SCARGILL, to be published (1959).
[2] P. G. M. BROWN, J. M. FLETCHER, C. J. HARDY, J. KENNEDY, D. SCARGILL, A. WAIN and J. WOODHEAD, *Second International Conference on the Peaceful Uses of Atomic Energy, Geneva* 15/P/31 (1958).
[3] K. ALCOCK, F. C. BEDFORD, W. H. HARDWICK and H. A. C. MCKAY, *J. Inorg. Nucl. Chem.* **4**, 100 (1957).
[4] F. L. MOORE, *Analyt. Chem.* **28**, 997 (1956).

benzene to remove traces of TTA, and air was bubbled through to remove traces of benzene. The solution was shown to contain <0·05% of ^{95}Zr by (i) a paper chromatographic method (described in detail below) and (ii) the standard radiochemical method of GLENDENIN,[5] which also showed that there was <0·01% of active rare-earths.

The ^{95}Zr in the TTA/benzene solution was purified by washing it with 2 M HNO_3 containing <1% hydrogen peroxide,[4] and extracted into 40% HF. The solution of ^{95}Zr was shown to contain <0·1% ^{95}Nb by the paper chromatographic method below.

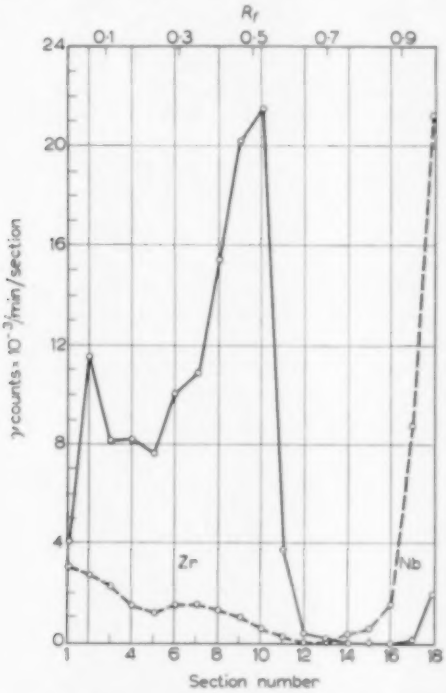

FIG. 1.—The separation of zirconium and niobium by paper chromatography; broken line: 34% ^{95}Zr/66% ^{95}Nb; full line: ^{95}Zr after ~1 day decay (1·7% ^{95}Nb).

(2) *The separation of* ^{95}Nb *and* ^{95}Zr *by a paper chromatographic-solvent extraction method*

The 0·5% oxalic acid solution of ^{95}Nb and ^{95}Zr was evaporated to dryness in a platinum crucible, and gently heated to destroy the oxalic acid. The residue was then dissolved in the minimum amount of 40% HF with warming to assist complete solution, and this stock solution kept in a polythene container.

The ^{95}Zr and ^{95}Nb in an aliquot of the fluoride solution were then separated by upward elution on a strip of Whatman No. 3 filter paper with a solvent mixture of 1 part of 40% HF and 1 part of methylethylketone in a covered polythene beaker (cf. the method by FUDGE and CROUTHAMEL[6]). According to the amount of activity required a single spot of 0·001 ml or a number of bands of 0·05 ml, can conveniently be eluted on the Whatman CRL type of sheet which has 10 strips 9 cm long × 1·5 cm wide separated by slots. A 0·001 ml spot of a more dilute ^{95}Zr/^{95}Nb solution was eluted simultaneously on one of the strips (the "pilot" strip) in order to determine the final position of the ^{95}Zr and ^{95}Nb activity. After elution for a distance of approximately 8 cm (30 min) the strips were dried

[5] L. E. GLENDENIN, C. D. CORYELL and N. SUGARMAN, *Radiochemical Studies on Fission Products* Book 3, p. 1523. McGraw-Hill, New York (1957).
[6] A. J. FUDGE and C. E. CROUTHAMEL, *J. Inorg. Nucl. Chem.* **5**, 240 (1958).

with a hair-drier, the "pilot" strip was divided into 18 sections and the γ activity of each section determined with a γ scintillation counter. The ^{95}Zr usually lies between the starting line and $R_f \sim 0{\cdot}7$, while the ^{95}Nb lies between $R_f \sim 0{\cdot}7$ and the solvent front. The sections between $R_f \sim 0{\cdot}6$ and $\sim 0{\cdot}8$ can be discarded (in case there is slight overlap of ^{95}Zr and ^{95}Nb) and pure ^{95}Zr and ^{95}Nb can be removed from the two sections $R_f = 0$–$0{\cdot}6$ and $0{\cdot}8$–$1{\cdot}0$ respectively.

The sections containing the ^{95}Zr were stirred for 2 min with 2 ml of 12 M HNO_3 containing 0·1 M aluminium nitrate, and 2 ml of 50% TBP in odourless kerosene or similar diluent. The solvent phase containing the ^{95}Zr was removed, diluted to 25% TBP with kerosene, and the ^{95}Zr stripped twice into 1 ml of 0·1 M HNO_3 (which gives 2 ml of approx. 2 M HNO_3). The aqueous phase was scrubbed with benzene to remove traces of TBP, and air was bubbled through to remove traces of benzene. This method gives a concentrated stock solution of ^{95}Nb-free ^{95}Zr in 2 M HNO_3 but it is recommended that only sufficient should be prepared for the day's requirements since $\sim$2% of ^{95}Nb grows per day from the decay of the ^{95}Zr and this amount can be very significant in solvent extraction experiments in which distribution coefficients $<0{\cdot}1$ or >10 are to be measured.

The ^{95}Nb may be recovered in a similar manner, using 50% TBP and 15 M HNO_3 containing 0·1 M $Al(NO_3)_3$ to extract the ^{95}Nb from the paper strip, followed by dilution of the solvent to 20% TBP, and back-extraction into water.

This chromatographic method can be used to determine the percentages of ^{95}Nb and ^{95}Zr in their mixtures in both aqueous and organic (e.g. TBP-kerosene) solutions. Good separation can be obtained if small aliquots ($<0{\cdot}005$ ml) are added to the strip, and if $\sim$0·1 ml of 40% HF is added to the strip at each side of (and touching) the spot, and allowed to dry before elution with the solvent mixture. It was observed that a trough occurred in the ^{95}Zr chromatogram and this may be due to a partial separation of more than one zirconium species. Typical chromatograms obtained for $\sim$2% ^{95}Nb in ^{95}Zr after a decay of one day, and also a mixture of 34% ^{95}Zr and 66% ^{95}Nb are shown in Fig. 1.

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ANNOUNCEMENT

PRELIMINARY NOTICE

Second International Congress of Polarography Organized by the Polarographic Society

To be held in Cambridge 24–29 August 1959

THE Congress will be held in the University of Cambridge and will consist of Scientific Sessions (original papers, reviews and discussions) and Exhibition of Commercial Equipment, Demonstrations of Laboratory Apparatus, visits to local industry and places of interest and social functions.

A supporting programme for ladies is being arranged.

The scientific programme will be divided into the following sections:—

(1) Instrumentation.
(2) Theory and Kinetics.
(3) Analytical and Industrial Applications.
(4) Fundamental Studies.
(5) Biological and Medical Applications.
(6) Miscellaneous.

There will also be four Plenary Lectures by World Authorities and six Section Lectures.

Contributions will be welcome and details should be submitted to: G. F. REYNOLDS, M.Sc., F.R.I.C., *Chemical Inspectorate, Ministry of Supply, C.*36. *Royal Arsenal, Woolwich, London, S.E.*18, *England.*

Notification of intention to submit a communication should be made as soon as possible and not later than 31 March 1959, by which date a summary not exceeding 200 words is also required.

Preprints of all papers will be issued and final manuscripts must therefore be received not later than 31 May 1959.

There will be an exhibition of commercial equipment and ancilliary materials.

Requests for application forms and further details should be sent to: Mrs. B. LAMB, B.Sc., F.R.I.C., *Chemistry Laboratory, Evershed and Vignoles, corner of Iveagh Avenue, North Circular Road, London, N.W.*10, *England.*

J. Inorg. Nucl. Chem., 1959, Vol. 9, p. 326. Pergamon Press Ltd. Printed in Northern Ireland

BOOK REVIEW

J. KOCH (Editor), R. H. V. M. DAWTON, M. L. SMITH and W. WALCHER: **Electromagnetic Isotope Separators and Applications of Electromagnetically Enriched Isotopes,** North-Holland Publishing Co., 1958. xi + 314 pp., £2. 15s. 6d.

WHILE there are a number of standard texts on mass spectrometry, this book gives the first general account of the techniques of electromagnetic isotope separation on a larger scale and of the applications of electromagnetically enriched isotopes. It is not written primarily for the small number of specialists concerned with the design and operation of separators but as a guide to the users of enriched isotopes and to the physicists who are interested in the potentialities of the equipment for their own laboratories. The justification of the book thus lies in the rapid increase in utilization of the isotopes over the past decade, the increasing demand for the information possessed by the few specialized groups operating separators, and the recent decisions by institutes in several countries to instal separators for assisting their own research programmes.

Generally the main interest in electromagnetic separation is in the provision of samples for research studies, the concern with techniques being limited to achieving the best efficiency and resolution, but there are also features of the electromagnetic process which are of special interest in wider fields such as the development of ion sources and the sputtering effects of ions arriving at the solid collector surfaces.

The present book, which attempts to cover all these aspects, consists of three main parts dealing, respectively, with the uses of laboratory instruments, with the large scale production units and applications of their products, and lastly, with a number of fundamental physical problems, which are of importance in separator design and have a special bearing on the future technological development. The book thus covers the whole field of electromagnetic separator theory and practice (apart from mass spectrometry) and also provides a unique guide to the extensive report and journal literature on the field. It is well known that the techniques of large scale production of enriched isotopes by electromagnetic separation were highly developed in the United States during the period of the Second World War. However, it was not until 1955 that the first general exchange of information in the field occurred in the conference at Harwell, an event which clearly demonstrated the usefulness of the machines to research especially in nuclear physics. The later exchange at the Amsterdam International Symposium on isotope separation further emphasised the value of electromagnetic isotope separation methods and in particular the application to plutonium.

Electromagnetically enriched isotopes are used in many fields of work particularly in nuclear studies, where the nuclear properties, such as neutron cross-sections, of different isotopes of a particular element may differ widely. Samples for study can either be obtained by direct deposition in the beam of the separator or, in larger quantities, can be processed chemically and supplied in a pure form for the user. The first two parts of the book give detailed accounts of both these techniques. This method of isotope separation can become of particular value in the separation of radioactive isotopes since the collected samples are well suited for beta and gamma spectrometer studies. Because of its versatility, too, the method is well suited to the provision of rare isotopes of the rarer elements.

The book is well produced and illustrated, has a detailed index, and should be of wide interest to scientists working with isotopes in many fields.

M. L. SMITH

J. Inorg. Nucl. Chem., 1959, Vol. 9, pp. 327 to 328. Pergamon Press Ltd. Printed in Northern Ireland

Papers to be published in future issues

V. Y. LABATON: The fluorides of uranium—IV. Kinetic studies on the fluorination of uranium tetrafluoride by chlorine trifluoride.

V. Y. LABATON and K. D. B. JOHNSON: The fluorides of uranium—III. Kinetic studies of the fluorination of uranium tetrafluoride by fluorine.

B. C. PURKAYASTHA and S. N. BHATTACHARYYA: The coprecipitation of rare earths with calcium oxalate.

A. T. CASEY and A. G. MADDOCK: The chemistry of protactinium—IV. Some spectrophotometric observations.

C. B. AMPHLETT, L. A. MCDONALD, J. S. BURGESS and J. C. MAYNARD: Synthetic inorganic ion-exchange materials—III. The separation of rubidium and caesium of zirconium phosphate.

R. W. JOHNSON and D. S. MARTIN, JR.: Kinetics of the oxidation of cerium(III) by concentrated nitric acid.

L. G. STONHILL: An apparatus for thermogravimetry in hazardous atmospheres.

J. MACKIN and D. LOVE: Branching fraction and half-life of potassium-42.

P. S. GENTILE, L. H. TALLEY and T. J. COLLOPY: The chemistry of uranyl nitrate–hydroxide–urea systems.

P. S. GENTILE, L. H. TALLEY and T. J. COLLOPY: Some evidence for the presence of uranic acid in uranium trioxide—Water systems.

S. WEXLER: Dissociation of TH and T_2 by beta decay.

A. C. WAHL: 14-Year ^{113m}Cd.

T. V. HEALY and J. KENNEDY: The extraction of nitrates by phosphorylated reagents—I. The relative extraction rates and solvating mechanisms for uranyl nitrate.

D. A. BROWN: Organometallic complexes—II. On the existence of some mononuclear and binuclear metal–organic complexes.

D. A. BROWN: Organometallic complexes—III. On the possible existence of metal–organic complexes containing hetero-atoms.

S. AMIEL and R. E. SEGEL: Search for ^{20}O.

R. A. SHARP and A. C. PAPPAS: ^{115}Cd Isomer yield ratios from deuteron fission of ^{238}U and from the ^{119}Sn(d, αp), ^{119}Sn(n, α), ^{115}In(d, $2p$), ^{115}In(n, p), and ^{114}Cd(d, p) reactions from 10 to 25 MeV.

W. P. GRIFFITH, F. A. COTTON and G. WILKINSON: The infra-red spectrum of $K_4[Ni(CN)_3CO]_2$.

W. HÜBEL und E. H. BRAYE: Organometallic complexes—IV. Über die Reaktion von substituierten Acetylenverbindungen mit Eisentetracarbonyl.

D. F. PEPPARD, G. W. MASON and R. J. SIRONEN: Isolation of neptunium as a mono octyl phosphoric acid complex by liquid–liquid extraction.

A. COTTON, R. R. MONCHAMP, R. J. M. HENRY and R. C. YOUNG: The preparation and properties of a new pentacyanomanganese–nitric oxide anion, $[Mn(CN)_5NO]^{-2}$, and some observations on other pentacyanonitrosyl complexes.

M. A. FINEMAN and R. DAIGNAULT: Electronegativaties calculated using a modification of Pauling's equation.

T. V. HEALY, J. KENNEDY and G. M. WAIND: The extraction of nitrates by polyphosphorylated reagents—II. The relative extraction rates of uranyl, cobaltous and sodium nitrates with phosphate esters.

T. MOELLER and G. W. CULLEN: Observations on the rare earths—LXIX. An electrochemical investigation of ethylenediamine solutions of lanthanum.

C. J. HARDY and D. SCARGILL: Studies on mono- and di-*n*-butylphosphoric acids—I. The separation of mono- and di-*n*-butylphosphoric acids by solvent extraction and by paper chromatography.

D. HALL and G. N. WALTON: Chemical effects in fission recoil—IV. The efficiency of recoiling atoms in the decomposition of potassium nitrate.

R. SKOCHDOPOLE and S. CHABEREK: Iron chelates of N-hydroxyethylethylenediaminetriacetic acid.

J. D. KNIGHT, D. C. HOFFMAN, B. J. DROPESKY and D. L. FRASCO: Radiations of ^{89}Y and ^{91}Y and half-lives of ^{89}Sr and ^{91}Sr.

E. Weiss and W. Hübel: Organometallic complexes—V. π-Komplexe ans cyclischen Dienverbindungen und Metallcarbonylen.

H. Irving and D. N. Edgington: The extraction of some metal chlorides into tri-*n*-butyl phosphate.

A. T. Casey and A. G. Maddock: The chemistry of protactinium—V. A comparison of the extraction of protactinium, niobium and tantalum.

J. Vandegaer, S. Chaberek and A. E. Frost: Iron chelates of diethylenetriaminepentaacetic acid.

R. Harder and S. Chaberek: The interaction of rare earth ions with diethylenetriaminepentaacetic acid.

S. Chaberek, A. E. Frost, M. A. Doran and N. J. Bicknell: Interaction of some divalent metal ions with diethylenetriaminepentaacetic acid.

D. F. Peppard and J. R. Ferraro: The preparation and infra-red absorption spectra of several complexes of bis-(2-ethylhexyl)-phosphoric acid.

D. Sen and W. C. Fernelius: Catalytic racemization of optically active complexes: tris(ethylenediamine)-cobalt(III), -platinum(IV) and -rhodium(III) halides.

W. N. Lipscomb: Structure and reactions of the boron hydrides.

D. A. Brown: The electronic structure of the complex $Fe_2C_{10}H_4O_8$.

F. Vrátný: Stress relaxation and exchange in pellets used for the infra-red technique.

J. R. Ferraro: The nature of the nitrate in the TBP solvates $M(NO_3)_3 \cdot 3TBP$, $M(NO_3)_4 \cdot 2TBP$ and $MO_2(NO_3)_2 \cdot 2TBP$.

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